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CONTENTS

RP	TITLE AND AUTHOR	Page
975.	Anodizing of aluminum alloys in chromic acid solutions of different concentrations. Robert W. Buzzard..... [Price 5c]	251
976.	Cooperative study of methods for the determination of oxygen in steel. John G. Thompson, Herbert C. Vacher, and Harry A. Bright..... [Price 10c]	259
977.	A new phenomenon in the superconducting transition of tantalum and of tin. Francis B. Silsbee, Russell B. Scott, and Ferdinand G. Brickwedde..... [Price 5c]	295
978.	Optical rotation and atomic dimension for the four optically active 1-halogeno-2-methylbutanes. Dirk H. Brauns..... [Price 5c]	315
979.	Simplified volumetric determination of alpha, beta, and gamma cellulose in pulps and papers. Herbert F. Launer..... [Price 5c]	333
980.	Reaction of wool with strong solutions of sulfuric acid. Milton Harris, Ralph Mease, and Henry Rutherford..... [Price 5c]	343
981.	Performance characteristics of a water current meter in water and in air. Galen B. Schubauer and Martin A. Mason..... [Price 5c]	351
982.	Soil-corrosion studies, 1934. Field tests of nonbituminous coatings for underground use. Kirk H. Logan and Scott P. Ewing [Price 10c]	361

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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP975

Part of Journal of Research of the National Bureau of Standards, Volume 18, March 1937

ANODIZING OF ALUMINUM ALLOYS IN CHROMIC ACID SOLUTIONS OF DIFFERENT CONCENTRATIONS

By Robert W. Buzzard

ABSTRACT

Investigation of the 3-percent chromic acid anodizing bath showed that the recommended voltage cycle was essential for formation of the best coatings. It was shown that not only could the corrosion-inhibiting properties of the coatings be improved by an increase in concentration of the electrolyte to 5 to 10 percent of chromic acid, but that the cycle could be eliminated, the time decreased, and the anodizing range of voltage and temperature broadened.

CONTENTS

	Page
I. Introduction	251
II. Procedure	251
III. Summary	256
IV. References	257

I. INTRODUCTION

The practical advantage of the so-called "anodic" coatings on aluminum alloys to increase the adhesion of paint [8] [1] has been well established and accepted for a number of years. Coatings of this kind are produced electrolytically by making the specimen the anode in a suitable electrolytic bath. The outstanding coating used for the above purpose for a number of years is that produced in an electrolyte of chromic acid. The only concentration of chromic acid used previous to the present investigation was that recommended by Bengough [3] in 1926. In this method a 3-percent (0.3 *M*) chromic acid solution was used for the electrolyte and a definite empirical voltage cycle was specified, a requirement that made the method an intermittent process. This requirement was a decided limitation in mass production and has been cited by proponents of other methods as the outstanding objection to the use of the chromic acid method. This limitation, coupled with the relatively early "break-down" of the bath, and the very narrow "anodizing" range of voltage and temperature, prompted the study here reported. The purpose of the investigation was to improve the method, both with respect to the stability of the solution and to the technique of the anodizing process.

II. PROCEDURE

Practical tests with the 3-percent chromic acid electrolyte demonstrated the necessity of close adherence to the recommended voltage cycle [2] and temperature (40° C) [3]. Sheet duralumin specimens were

[1] The numbers in brackets refer to the literature references at the end of this paper.

[2] 0 to 40 volts in 15 minutes, 35 minutes at 40 volts, 5 minutes from 40 to 50 volts, and 5 minutes at 50 volts.

anodized in this solution under the recommended conditions. Comparison specimens were anodized in the same bath at a constant potential of 40 volts at 40° C for 1 hour. Visual examination of the resultant coatings showed only slight differences in surface characteristics, for example, the coating produced at a constant voltage was darker in color and had a softer surface, which adhered slightly to the fingers on rubbing. The specimens coated by the recommended voltage cycle showed superior corrosion-resistance in laboratory salt-spray tests,[3] as is shown in figure 1. Both coatings complied with the

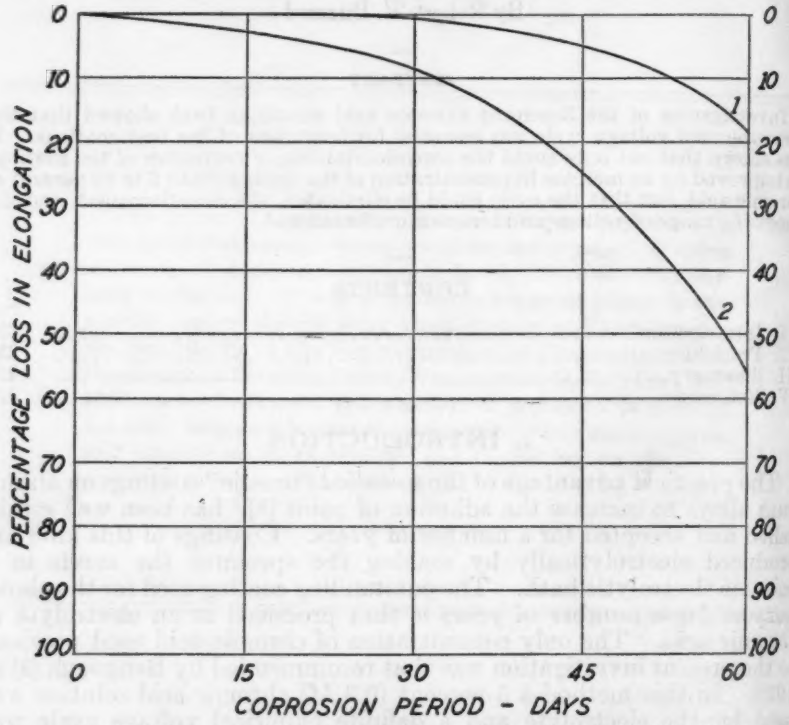

FIGURE 1.—*Relative corrosion-resistance of anodic coatings formed in the 3-percent chromic acid baths, and corroded in the 20-percent* NaCl *spray.*

(1) Film formed with the Bengough cycle.
(2) Film formed 40 volts at 40° C for 1 hour.

Navy Department specification [10] covering acceptance tests for anodized duralumin, that is, a loss of not more than 10 percent in elongation after a 30-day salt-spray test. However, at the end of a 60-day corrosion period, the specimens coated by using the recommended voltage cycle lost less than half as much of their elongation in tensile tests as did the companion specimens, which were coated under constant-voltage conditions. The data on the corrosion-resistance of the coatings represent the percentage decrease in elongation in tensile tests, following exposure, either to a salt spray with a 20-percent sodium chloride solution, at 35° C, or to intermittent immersion in a

[3] The salt-spray tests were run at a constant temperature of 35° C. The 20-percent NaCl solution was made up with Cp NaCl and distilled water. The solution was filtered before use. The concentration of the solution was checked daily by gravity determinations.

solution containing 9 parts of normal NaCl and 1 part of 3-percent H_2O_2 at room temperature.

It was found that the quality of the coating and the conditions under which the process could be carried out satisfactorily varied with the chromic acid concentration of the bath. Specimens anodized in 5-percent (0.5 *M*) chromic acid at a constant voltage for 1 hour were found to compare favorably in corrosion resistance to the best coatings produced in the 3-percent chromic acid bath. The increase in concentration of chromic acid so changed the bath characteristics that the voltage cycle was not needed. An increase of the chromic acid concentration up to 10 percent (1 *M*) produced further improvement in

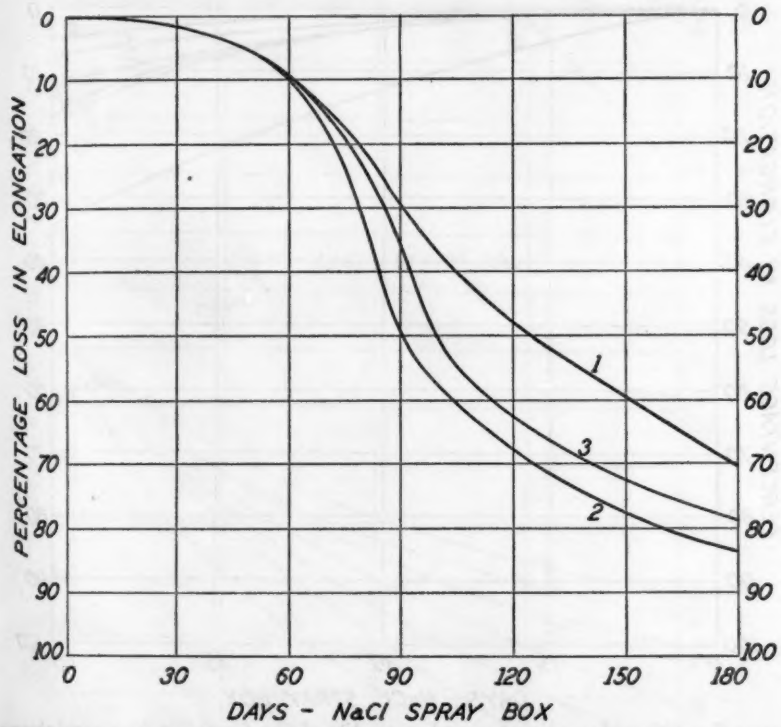

FIGURE 2.—*Comparative corrosion resistance of anodic films formed in varying concentrations of chromic acid and corrodea i ı the 20-percent* NaCl *spray.*

(1) 10-percent chromic acid bath; 40 volts at 35° C for 1 hour.
(2) 5-percent chromic acid bath; 40 volts at 35° C for 1 hour.
(3) 3-percent chromic acid bath with Bengough cycle.

both the quality of the coating and in the operating conditions. The improvement in the quality of the coating is illustrated by the three curves in figure 2.

The elimination of the empirical voltage cycle for the anodizing treatment by the use of higher concentrations of chromic acid permitted the process to be run continuously. This eliminated one of the major limitations previously encountered in anodizing in chromic acid solutions.

In general, the permissible ranges of temperature and voltage for anodizing were greatly broadened by use of the 10-percent chromic acid

solution. With the 5-percent chromic acid solution no variation in voltage was permissible, whereas, with the 10-percent solution, satisfactory results were obtained by using any constant potential within the range from 30 to 40 volts. The effect of time, that is, the length of the anodizing period, on the quality of the coatings [4] produced at 30 and at 40 volts, respectively, was studied in the 10-percent chromic acid solution at 35° C. After anodizing, the coated sheet duralumin specimens were subjected to the salt-spray test for 60 days. It is evident from the results in figure 3 that treatment for periods of 30 minutes or longer at either 30 or 40 volts in a 10-percent chromic acid bath at 35° C produced excellent protective coatings. It is also

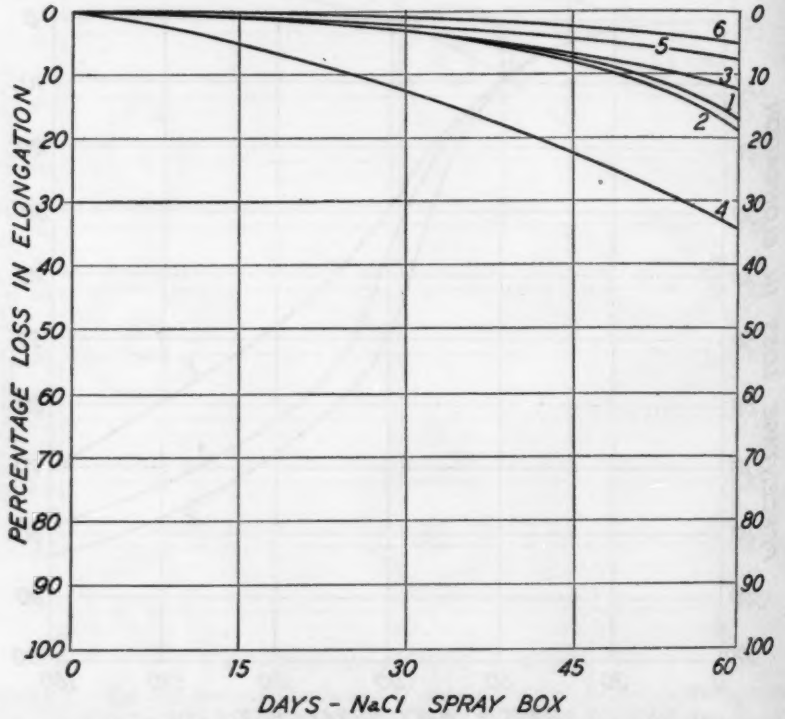

FIGURE 3.—*Effect of anodizing period on quality of film formed in 10-percent chromic acid and corroded in the 20-percent* NaCl *spray.*

Films formed at 40 volts and 35° C for:
(1) 15 minutes.
(2) 30 minutes.
(3) 60 minutes.

Films formed at 30 volts and 35° C for:
(4) 15 minutes.
(5) 45 minutes.
(6) 60 minutes.

apparent that, for the longer anodizing periods, 30 volts gave a better coating than did 40 volts. For producing coatings having maximum corrosion resistance, a 60-minute anodizing period should be used, although treatment for 30 minutes in the 10-percent chromic acid bath produced coatings which satisfactorily met the requirements of the Navy specification [10].

The comparative merits of anodic coatings produced in a 10-percent chromic acid solution, and of similar coatings produced in a 3-percent solution, are portrayed in figure 4. The upper series of curves sum-

[4] Anodized at Naval Aircraft Factory, Philadelphia, in a large commercial installation.

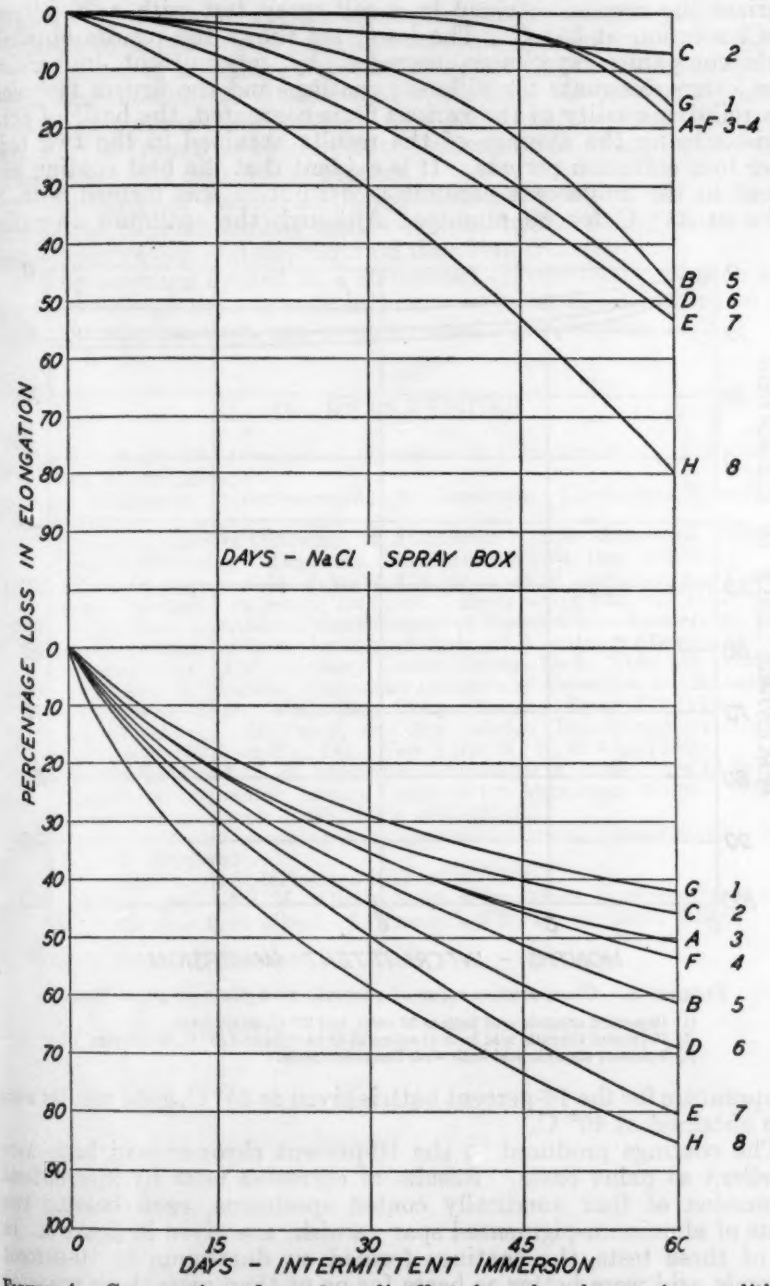

FIGURE 4.—*Comparative values of anodic films formed under varying conditions.*

(a) 3-percent chromic acid bath with Bengough cycle.
(b) 3-percent chromic acid bath at 40 volts and 40° C.
(c) 10-percent chromic acid bath at 35 volts and 40° C.
(d) 10-percent chromic acid bath at 30 volts and 30° C.
(e) 10-percent chromic acid bath at 38 volts and 30° C.
(f) 10-percent chromic acid bath at 40 volts and 35° C.
(g) 10-percent chromic acid bath at 30 volts and 35° C.
(h) 10-percent chromic acid bath at 35 volts and 35° C.

The letters represent the relative quality of the coatings, based on the average of the results of the two corrosion tests for four intervals.

marizes the results obtained in a salt-spray test with a 20-percent NaCl solution at 35° C. The lower set shows the results obtained with companion specimens corroded by intermittent immersion. The letters designate the different coatings and the figures represent the relative quality of the various films compared, the basic of comparison being the average of the results obtained in the two tests after four corrosion periods. It is evident that the best coating produced in the 10-percent chromic acid solution was formed with 30 volts at 35° C for 60 minutes. Although the optimum operating

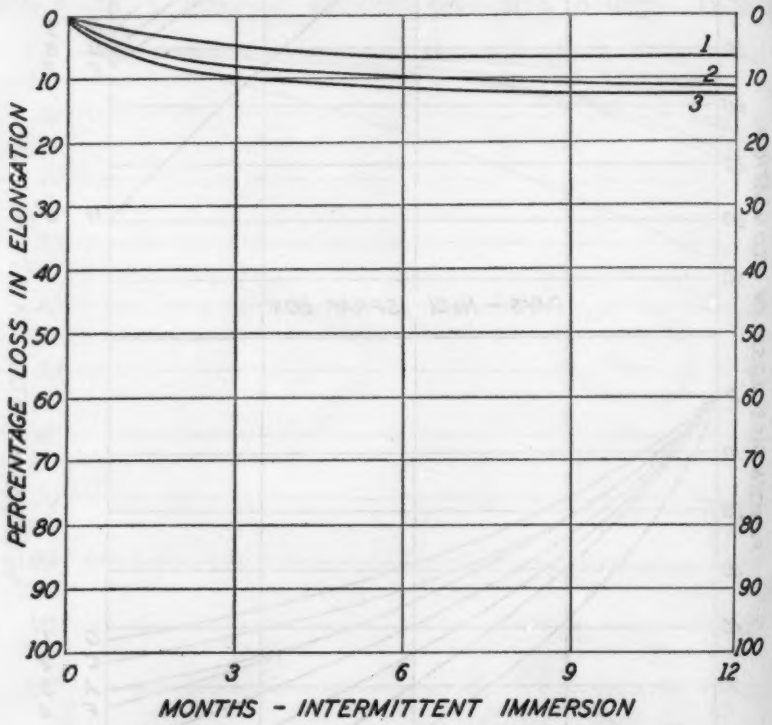

FIGURE 5.—*Comparative value of chromic acid films as paint bases.*

(1) 10-percent chromic acid bath at 30 volts, and 35° C, 60 minutes.
(2) 10-percent chromic acid bath at either 35 or 40 volts and 35° C, 60 minutes.
(3) 3-percent chromic acid bath with Bengough cycle.

temperature for the 10-percent bath is given as 35° C, good results were also obtained at 40° C.

The coatings produced in the 10-percent chromic acid bath were excellent as paint bases. Results of corrosion tests by intermittent immersion of four anodically coated specimens, each bearing two coats of aluminum-pigmented spar varnish, are given in figure 5. In all of these tests, the coatings formed on duralumin in 10-percent chromic acid were better as bases for paint than were those prepared in 3-percent chromic acid.

III. SUMMARY

1. The necessity for using the empirical voltage cycle recommended for anodizing baths containing 3 percent of chromic acid has been

verified. However, by increasing the chromic acid concentration from 3 percent to either 5 or 10 percent, this cycle is no longer necessary.

2. The use of a voltage cycle in processes of this kind necessarily limits the method to intermittent operation. Good coatings have been formed at constant voltages by using a more concentrated solution, that is, from 5 to 10 percent of chromic acid. This method may be operated as a continuous process.

3. The range of voltage and temperature over which the anodizing process can be satisfactorily used is widened by increasing the chromic acid concentration and the required time is decreased.

4. The coatings formed in a 10-percent chromic acid solution at a constant voltage are superior in many ways to those formed in the 3-percent solution with the recommended voltage cycle.

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[2] Carl Comments, *Protective coatings for aluminum.* Chem. Met. Eng. **31,** 698 (1924).
[3] Anonymous, Anodic Oxidation of Aluminum and its Alloys as a Protection Against Corrosion. Dept. Sci. Ind. Research Brit. Rep. (1926).
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[7] J. D. Edwards, F. C. Frary, and Zay Jeffries, The Aluminum Industry. (McGraw-Hill Book Co., Inc., New York, N. Y., **2,** 476, 1930).
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[10] Navy Department Specification SR19c (1936).
[11] R. W. Buzzard and J. H. Wilson, *Solution breakdown in chromic acid anodic baths for aluminum alloys.* J. Research NBS **18,** 53 (1937) RP961.

WASHINGTON, December 22, 1936.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP976

Part of Journal of Research of the National Bureau of Standards, Volume 18, March 1937

COOPERATIVE STUDY OF METHODS FOR THE DETERMINATION OF OXYGEN IN STEEL

By John G. Thompson, Herbert C. Vacher, and Harry A. Bright

ABSTRACT

The data from reports of 35 laboratories, comprising more than 2,000 analytical determinations, indicate that the vacuum-fusion method yields accurate results for the oxygen contents of plain-carbon steels either aluminum-killed, silicon-killed, or of the rimming type; the aqueous-iodine method yields accurate results for some types of killed steels and low results for other steels; more data, and particularly more concordant data, are necessary to define the accuracy of the other methods employed in this cooperative analysis.

The vacuum-fusion procedures are reviewed and recommendations given for obtaining optimum results by this method.

CONTENTS

	Page
I. Introduction	259
II. Review of the results obtained in the cooperative analyses	265
1. Vacuum-fusion method	265
(a) Recommendations for the determination of oxygen by the vacuum-fusion method	270
(b) Determinations of nitrogen and hydrogen	271
2. Iodine method	272
3. Accuracy of the vacuum-fusion and aqueous-iodine methods	279
4. Hydrogen-reduction method	281
5. Electrolytic method	282
6. Miscellaneous methods	287
(a) Mercuric-chloride method	290
(b) Chlorine method	290
(c) Fractional vacuum-fusion method	291
(d) Nitric-acid method	291
(e) Hydrochloric-acid method	292
III. Authors' comments and conclusions	292

I. INTRODUCTION

The methods employed for the determination of oxides and oxygen in ferrous materials may be roughly classed in two groups, "residue" methods and "reduction" methods. The first group includes the iodine, electrolytic, mercuric chloride, hydrochloric acid, nitric acid, and chlorine methods, all depending upon the action of a selected medium to separate the metallic portions of the sample from the oxygen-containing constituents. Subsequent analysis of the insoluble residue permits the isolation and separate determination of individual oxides and compounds. The reduction methods depend upon the action of carbon or hydrogen, at elevated temperatures, to reduce the oxygen-containing constituents. With the exception of the recently

developed fractional vacuum-fusion method, the reduction methods do not attempt to identify individual oxides and compounds but yield only a single value for the sum of the oxygen contents of several or all of the oxide constituents. With such a diversity in principles and aims, it is not surprising that concordance of results by different methods has usually been difficult to obtain and, consequently, the accuracy and merits of each of the methods of analysis have been subjects of controversial and extended discussion.

The present cooperative attempt to define the accuracy and limits of usefulness of the various methods originated in correspondence between Dr. John Johnston, Director of Research of the United States Steel Corporation, and other metallurgists. The plan was, briefly, to submit identical samples to a number of laboratories for analysis by different methods and to collate the results of these analyses. The project was endorsed by the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers at the Annual Meeting in February 1933, and has been conducted under the joint sponsorship of the Iron and Steel Division and the National Bureau of Standards. The latter organization undertook the preparation and distribution of sample material and the collection of data from the cooperating laboratories. The preliminary stages of the undertaking have been described in progress reports [1] to the sponsors. The results obtained to date, comprising more than 2,000 individual determinations, are described in considerable detail in a paper [2] presented at the meeting of the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers in February 1937 and are presented in somewhat condensed form in the present paper, together with a few data that were not available when the other report was prepared.

Seven plain-carbon steels and one open-hearth iron were selected, chiefly from commercially available material, covering a range in carbon, silicon, manganese, sulphur, phosphorus, and oxygen contents. Different melting and deoxidation practices insured the presence in the different steels of different amounts and combinations of oxygen. Alloy steels were not included in the selected list, to avoid the additional complications introduced by the presence of alloying elements. The seven steels and the open-hearth iron recorded in table 1 were procured by R. F. Mehl and C. H. Herty, Jr., through the cooperation of the Jones and Laughlin Steel Corporation, the Carnegie Steel Co., and the American Rolling Mill Co.

Many precautions were observed in the preparation of sample material in order that all of the analytical samples of a particular steel should be as nearly identical as possible. For each of the eight compositions a portion of a single large ingot was selected so as to obtain material as free as possible from vertical segregation. Difficulties resulting from horizontal segregation in the ingot, i. e., from skin to core, were avoided by converting the 500-pound selected portion of the ingot into hot-rolled rod approximately 1 inch in diameter. An analytical sample consisting of a complete cross section of a rod therefore represents a complete cross section of the ingot, and adjacent samples should be identical even though neither one is completely homogeneous.

[1] Mining and Met. 15, 215 (1934); 16, 184 (1935).
[2] Metals Tech. (December 1936).

TABLE 1.—*Type and composition of the selected steels*

TABLE 1.—*Type and composition of the selected steels*

Steel	Type	Additions			Composition (percent)						
		Furnace	Ladle	Mold	C	Si	Mn	S	P	Cr	V
1	Low-carbon, rimming	None	FeMn	None	0.03	0.002	0.31	0.036	0.011	0.004	<0.001
2	Medium-carbon, high-manganese, silicon-killed	FeMn	Hot metal, FeMn, FeSi	None	.42	.26	1.15	.025	.020	.022	<.001
3	Bessemer screw stock semikilled	None	FeMn, S	FeSi	.12	.024	.72	.168	.101	.006	.004
4	Special, low-carbon, aluminum-killed	SiMn, FeMn	FeSi, Al	None	.17	.09	.65	.029	.014	.008	.001
5	Low-carbon, silicon-killed	None	FeMn, FeSi	None	.22	.14	.45	.042	.020	.020	.001
6	Medium-carbon, silicon-killed	Spiegel	FeMn, FeSi	None	.43	.20	.47	.027	.014	.012	.001
7	Open-hearth iron, rimming	None	Al	None	.016	.001	.024	.022	.011	.009	<.001
8	Similar to no. 4, but higher in oxygen	None	Al	Al	.20	.03	.45	.033	.014	.012	<.001

Samples taken at intervals throughout the length of each rod were subjected to analysis by the vacuum-fusion method. These exploratory analyses confirmed the reproducibility of results obtained from adjacent specimens and showed that the oxygen content of the portion of each rod selected for sample material was satisfactorily uniform from end to end. The maximum difference between the highest and lowest values for each of the seven steels (oxygen content 0.02 percent or less) was 0.003 percent, and for the open-hearth iron (oxygen content 0.10 percent or more) the maximum difference was 0.01 percent.

For further study of segregation, transverse sections taken at intervals along each rod were roughly polished with 1G emery paper and then etched from 10 to 15 minutes in diluted hydrochloric acid (1+1) at 70° C. The characteristic pattern developed in each of the eight steels, figure 1, clearly indicated differences between the core and outer areas of most of the steels, but no significant difference could be detected in samples from different positions in the same rod. Oxygen segregation sometimes accompanies the segregation revealed by deep etching, as was shown by vacuum-fusion analyses of samples representing (1) complete cross sections of the rods, and (2) core areas after removal of the outer layers in a lathe. For example, the results for steel 1 were 0.019 percent of oxygen for the complete cross section 0.96 inch in diameter, and 0.033 percent of oxygen for the core area 0.357 inch in diameter. Likewise, the results for iron 7 were 0.112 percent of oxygen for the complete cross section 1.25 inches in diameter and 0.128 percent of oxygen for the core 0.494 inch in diameter. These results emphasize the necessity for using a complete cross section of a rod for each analytical sample.

Obviously the oxygen-rich scale resulting from hot-rolling must be removed from the sample prior to the determination of oxygen or oxides. To insure uniformity in this respect it was directed that the diameter of iron 7 be reduced to 1.25 inches and the diameter of each of the other steels to 0.95 inch, in a lathe just before the analytical samples were prepared.

At the completion of the exploratory examination the rods were cut into short lengths, each being marked to identify its position in the original rod. Bundles of eight 6-inch rods, one from each of the eight steels, were prepared for the cooperating laboratories.

Meanwhile correspondence had been conducted with laboratories in this country and abroad, that were known to be interested in the determination of oxygen in ferrous materials. The present summary is based on the results reported by the 35 laboratories listed in table 2, together with identification numbers and with indications of the methods of analysis employed. Several of the laboratories reported results by more than one method of analysis. Consequently, there are available 15 reports of determinations by the vacuum-fusion method, 11 by iodine methods, 8 by electrolytic methods, 4 by hydrogen-reduction methods, 3 by the chlorine method, 2 each by the mercuric-chloride and hydrochloric-acid methods, and one by the nitric-acid method, representing a total of more than 2,000 analytical determinations.

Research Paper 976

Journal of Research of the National Bureau of Standards

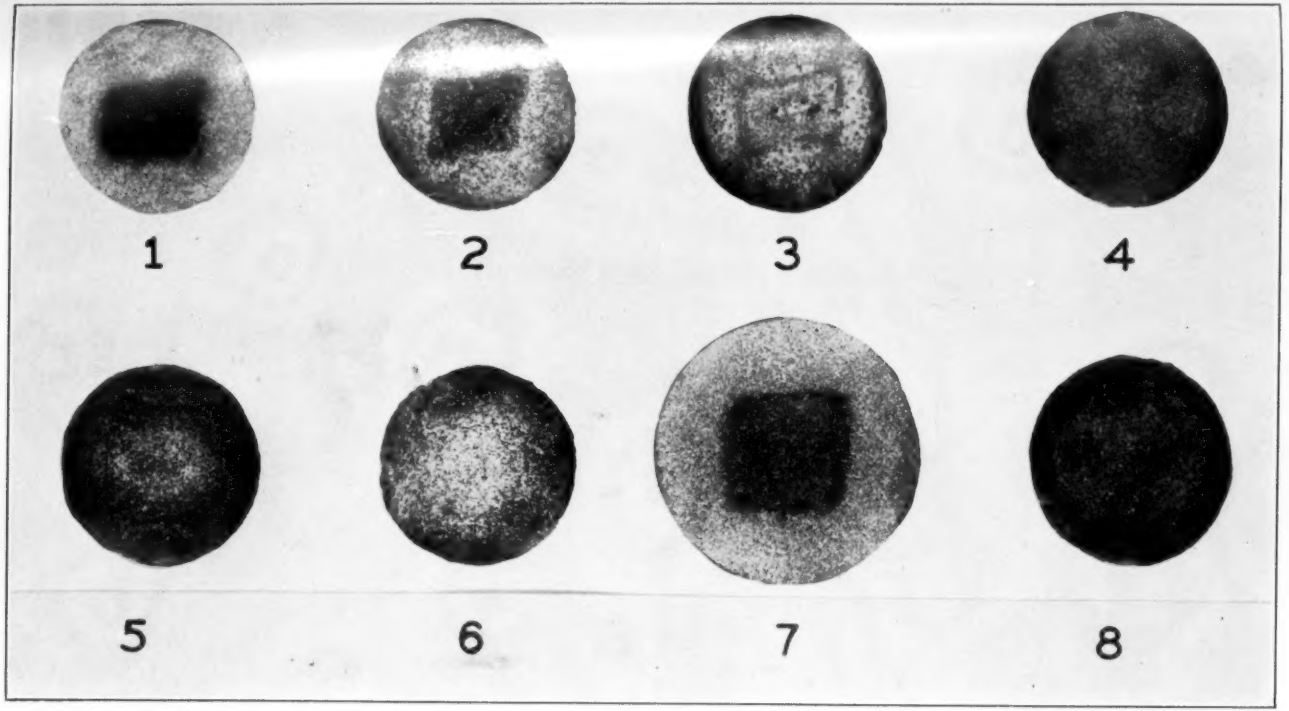

FIGURE 1.—*Appearance of the eight steels after deep etching in 1:1 hydrochloric acid.* ×1.

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TABLE 2.—*Cooperating laboratories and methods employed*

Identification number	Laboratory	Method
1	Battelle Memorial Institute, Columbus, Ohio. S. Epstein, Metallurgist.	Microscopical examination and inclusion count. Metals & Alloys **2**, 186 (1931).
2	United States Steel Corporation, Kearny, N. J. John Johnston, Director of Research; T. E. Brower, B. M. Larsen.	Hydrogen-reduction method. Trans. Am. Inst. Mining Met. Engrs. **113**, 61 (1934).
3	Mining and Metallurgical Advisory Boards to the Carnegie Institute of Technology, Pittsburgh, Pa. C. H. Herty, Jr., Director of Research; J. F. Sanderson, B. E. Sockman.	Electrolytic method as described by Fitterer, et al. U. S. Bur. Mines, Report of Investigations 3205 (May 1933).
4	Inland Steel Co., Indiana Harbor, Ind. Frank W. Scott.	Electrolytic method. Ind. Eng. Chem., Anal. Ed. **4**, 121 (1932).
5	The British (Guest Keen Baldwins) Iron and Steel Co., Ltd., Port Talbot, Wales. F. F. Hunting, Chief Metallurgist; N. Gray, Chief Chemist.	Hydrogen-reduction method. Sample melted with antimony and tin.
6	The Babcock and Wilcox Tube Co., Beaver Falls, Pa. Newell Hamilton, Research Metallurgist.	Vacuum-fusion method. Trans. Am. Inst. Mining Met. Engrs. **113**, 111 (1934).
7	Bethlehem Steel Co., Inc., Bethlehem, Pa. P. E. McKinney, Metallurgical Engineer; George F. Stammler.	Iodine method, essentially that of cooperator 13.
8	Department of Engineering Research, University of Michigan, Ann Arbor, Mich. John Chipman, Research Engineer; M. G. Fontana, C. L. Raynor.	Vacuum-fusion method. Ind. Eng. Chem., Anal. Ed. **7**, 391 (1935).
9	English Steel Corporation, Ltd., Sheffield, England. T. R. Walker, Chief Research Chemist.	Iodine method of cooperator 13 Nitric acid residue method. J. Iron Steel Inst. **113**, 177 (1926).
10	Lukens Steel Co., Coatesville, Pa. Wm. G. Hampton, Metallurgical Engineer.	Iodine method. Solution by Willems' method. Arch. Eisenhüttenw. **1**, 655 (1928); analysis of residue by method of cooperator 13.
11	The Research Institute for Iron, Steel, and Other Metals, Sendai, Japan. T. Ishiwara, Director; T. Yajima.	Vacuum-fusion method. Includes features of several procedures.
12	S K F Industries, Inc., Philadelphia, Pa. Haakon Styri, Director of Research.	Electrolytic method. Trans. Am. Inst. Mining Met. Engrs. **105**, 185 (1933); Metals & Alloys **5**, 96 (1934).
13	Electro Metallurgical Co., Niagara Falls, N. Y. Thos. R. Cunningham.	Iodine method of Cunningham and Price. Ind. Eng. Chem., Anal. Ed. **5**, 27 (1933).
14	Bell Telephone Laboratories, New York, N. Y. J. H. Scaff.	Vacuum-fusion method. Metals & Alloys **4**, 7 (1933).
15	Kaiser-Wilhelm Institut für Eisenforschung, Düsseldorf, Germany. F. Körber, Director.	Vacuum-fusion method. Mitt. Kaiser-Wilhelm Inst. Eisenforsch. **13**, 215 (1931). Chlorine method. Mitt. Kaiser-Wilhelm Inst. Eisenforsch. **9**, 195 (1927).
16	Ontario Research Foundation, Toronto, Canada. O. W. Ellis, Director of Metallurgical Research; J. R. Gordon, Research Metallurgist.	Iodine method of cooperator 13.
17	Kohle u. Eisenforschung GMBH Forschungsinstitut, Dortmund, Germany. E. H. Schulz, Director.	Chlorine method. Mitt. Forsch. Inst. Ver. Stahlwerke **1**, 231 (1930); Chem. Fabrik **2**, 51 (1929). Hydrogen-reduction method. Stahl u. Eisen **40**, 812 (1920); Arch. Eisenhüttenw. **3**, 459 (1929–30).
18	Metallografiska Institute, Stockholm, Sweden. Carl Benedicks, Director; G. Phragmén, Metallographer.	Vacuum-fusion method. Jernkontorets Ann. **114**, 549 (1931).
19	The American Rolling Mill Co., Middletown, Ohio. A. H. Thomas, Supervisor, Service Testing Laboratories; D. L. Reck, Research Engineer; O. B. Ellis, Chemist.	Electrolytic method of cooperator 3. Iodine method of cooperator 13.
20	Fried. Krupp Aktiengesellschaft Guszstahlfabrik, Essen, Germany. P. Klinger, Chief Chemist.	Vacuum-fusion method, presumably. Arch. Eisenhüttenw. **6**, 189 (1932). Analysis as described in Stahl u. Eisen **45**, 1559 (1925). Chlorine method. Arch. Eisenhüttenw. **7**, 618 (1933-34). Mercuric-chloride method. Arch. Eisenhüttenw. **8**, 391 (1934-35). Electrolytic methods. (A) Ind. Eng. Chem., Anal. Ed. **4**, 121 (1932). (B) Jernkontorets Ann. **116**, 166 (1932).

TABLE 2.—*Cooperating laboratories and methods employed*—Continued

Identification number	Laboratory	Method
21	Istituto Scientifico Tecnico Ernesto Breda, Milano, Italy.	Vacuum-fusion method. Arch. Eisenhüttenw. **6**, 189 (1932). Iodine method. Essentially method of cooperator 13.
22	The United Steel Companies, Limited, Stocksbridge, England. T. Swinden, Director of Research.	Iodine method of Rooney and Stapleton. J. Iron Steel Inst. **131**, 249 (1935).
23	Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa. T. D. Yensen, Manager, Magnetic Division; Wilson Scott, N. A. Ziegler.	Vacuum-fusion method. Trans. Am. Electrochem. Soc. **62**, 109 (1932).
24	A. O. Smith Corporation, Milwaukee, Wis. S. L. Hoyt, Director of Metallurgical Research; M. A. Schell, Research Metallurgist.	Fractional vacuum-fusion method. Trans. Am. Inst. Mining Met. Engrs. **113**, 82 (1934). Microscopical examination. Trans. Am. Inst. Mining Met. Engrs. **116**, 405 (1935).
25	The Babcock and Wilcox Co., Barberton, Ohio. J. B. Romer, Chief Chemist.	Mercuric-chloride method. Arch. Eisenhüttenw. **8**, 391 (1934-35).
26	School of Mines, Columbia University, New York, N. Y. William Campbell, Professor of Metallurgy; S. W. Poole.	Microscopical examination.
27	Department of Metallurgy, The University of Sheffield, Sheffield, England. J. H. Andrew, Professor of Metallurgy.	Iodine and vacuum-fusion methods. Iron and Steel Inst., 6th Report of the Heterogeneity of Steel Ingots, section I, p. 50, 61 (1935).
28	The Youngstown Sheet and Tube Co., Youngstown, Ohio. G. A. Reinhardt, Director of Research and Metallurgy; Francis M. Walters, Jr., Research Engineer.	Vacuum-fusion method. BS J. Research **7**, 375 (1931) RP346.
29	National Bureau of Standards, Washington, D. C. H. S. Rawdon, Chief, Division of Metallurgy; J. G. Thompson, H. C. Vacher, H. A. Bright.	Vacuum-fusion method. BS J. Research **7**, 375 (1931) RP346. Iodine method of cooperator 13. Hydrochloric-acid residue method. BS J. Research **9**, 615 (1932) RP496.
30	War Department, Watertown Arsenal, Watertown, Mass. G. F. Jenks, Col., Ordnance Department, U. S. Army, Commanding Officer; A. Sloan, P. R. Kosting, M. B. Gruzdis.	Iodine method of cooperator 13. Electrolytic method of cooperator 3.
31	The National Physical Laboratory, Teddington, England. C. H. Desch, Superintendent, Metallurgy Department.	Iodine method of Rooney and Stapleton. J. Iron Steel Inst. **131**, 249 (1935). Vacuum-fusion method. Sloman, Iron and Steel Inst., 6th Report of the Heterogeneity of Steel Ingots, section **4**, p. 71 (1935). Hydrogen-reduction method. Report of the Central Inst. Metals **14**, 449 (1935).
32	Central Institute of Metals, Leningrad, U S S R. B. Selivanoff, General Scientific Manager; Gr. Weinberg, Metallurgist; M. Janowsky, Chief of the Chemical Laboratories.	
33	Illinois Steel Co., Chicago, Ill. M. A. Grossman, Director of Research; Miss M. Baeyertz.	Microscopical examination.
34	Institut für Eisenhüttenkunde der Technischen Hochschule, Aachen, Germany. W. Eilender, Director.	Vacuum-fusion method, graphite-spiral furnace.
35	The Timken Steel and Tube Co., Canton, Ohio. Weston Hare.	Electrolytic method of cooperator 4. Hydrochloric-acid method.

The critical review of such a mass of data obviously can be better and more authoritatively accomplished by a small group, comprising experts in the various methods of analysis, rather than by one or two individuals. A subcommittee of the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers was therefore appointed, consisting of

John Chipman, chairman (American Rolling Mill Co.).
J. J. Egan (Union Carbide and Carbon Research Laboratories).
C. H. Herty, Jr. (Bethlehem Steel Co.).
S. L. Hoyt (A. O. Smith Corporation).
John Johnston (United States Steel Corporation).

On May 14, 1936, the committee, with Messrs. Hoyt and Johnston represented, respectively, by M. A. Scheil and B. M. Larsen, met with representatives of the National Bureau of Standards (J. G. Thompson, H. C. Vacher, and H. A. Bright) and with the following, who were present by invitation:

Thos. R. Cunningham (The Electro Metallurgical Co.).
Frank W. Scott (Inland Steel Co.).
O. B. Ellis (American Rolling Mill Co.).
Louis Jordan (Assistant Secretary, American Institute of Mining and Metallurgical Engineers).

To facilitate the review of the data the committee was divided into two sections. Messrs. Chipman, Larsen, Scheil, Jordan, Vacher, and Thompson considered the data of the vacuum-fusion, hydrogen-reduction, and chlorine methods, and Messrs. Herty, Egan, Cunningham, Scott, Ellis, and Bright reviewed the data of the extraction and residue methods. After 2 days of intensive study the two sections combined for general discussion. The results of these deliberations are given in the ensuing pages of this report, the various methods being discussed in order of the number of data available for each method.

II. REVIEW OF THE RESULTS OBTAINED IN THE COOPERATIVE ANALYSES

1. VACUUM-FUSION METHOD

The principles upon which the vacuum-fusion method, for the determination of total oxygen in iron or steel, is based are briefly as follows:

The sample is melted in a graphite crucible contained in a highly evacuated furnace. Under these conditions, occluded and dissolved oxygen is liberated and the various oxide and silicate combinations that exist in ferrous materials are reduced. In the usual procedure, determination of the amount of carbon monoxide in the evolved gases furnishes a value for the total oxygen content of the material but does not indicate the relative amounts of the different compounds of oxygen that were present. In the recently developed fractional vacuum-fusion method, values for individual oxides are obtained by reduction of the sample in stages at successively increased temperatures, with separate analysis of the gases evolved in each stage. The vacuum-fusion method permits the simultaneous determination of nitrogen and hydrogen, as well as oxygen, in a single sample.

Fifteen reports of determinations by the vacuum-fusion method were available for consideration. Some of the cooperators reported the results of individual determinations, others reported only one value for each steel. The preferred values of each cooperator, or averages of all the determinations in those instances where a preferred value was not indicated, are shown in table 3. Some of the averaged values have been rounded to eliminate meaningless fractions of one thousandth of 1 percent.

TABLE 3.—*Results obtained by the vacuum-fusion method*

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Iron 7		Steel 8	
Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator
%		%		%		%		%		%		%		%	
0.0215	6	0.018	15	0.0235	23	0.0055	6	0.014	23	0.0085	6	0.125	31	0.022	6
.021	14	.0175	27	.023	27	.005	24	.013	6	.008	29	.112	15	.022	27
.021	28	.016	29	.021	24	.004	15	.012	24	.0075	28	.110	6	.0195	23
.020	20	.016	18	.020	31	.004	27	.011	29	.007	15	.110	8	.019	15
.020	31	.016	31	.0195	29	.003	20	.0105	27	.006	24	.107	29	.019	31
.0195	24	.014	24	.019	15	.0025	28	.010	15	.006	27	.107	14	.0185	28
.019	34	.014	34	.017	8	.0025	18	.010	31	.0055	8	.107	34	.018	14
.019	29	.013	8	.017	14	.0025	14	.0085	8	.0055	18	.105	28	.017	29
.018	15	.013	20	.0145	28	.002	29	.008	18	.005	21	.105	18	.017	18
.018	23	.013	28	.014	21	.002	31	.0075	21	.005	34	.103	24	.016	8
.0175	11	.0125	11	.014	18	.0018	34	.007	14	.005	31	.103	23	.0155	24
.017	8	.012	21	.014	20	.0015	8	.007	20	.005	20	.100	21	.015	20
.016	18	.0115	6	.013	11	.001	21	.0065	11	.004	14	.100	20	.0145	34
.0145	21	.0115	23	.0115	6	.001	11	.0065	28	.003	11	.100	27	.0145	21
.009	27	.004	14	.011	34	.0000	23	.0065	34	.003	23	.096	11	.014	11
BEST VALUES															
0.018	------	0.017	------	0.017	------	0.002	------	0.009	------	0.007	------	0.106	------	0.017	------

The review of the vacuum-fusion data proceeded along three lines:

1. Arbitrary establishment of a range of acceptable results for each steel, by eliminating scattered high and low values.
2. Statistical study to determine the apparatus and procedures most consistently yielding results within the acceptable ranges.
3. Detailed study of apparatus and procedure of each cooperator for possible explanation of the failures to obtain consistently acceptable results.

In many cases, final conclusions were based upon consideration of all the foregoing criteria, but for convenience in this report the three items will be discussed separately.

The first impression was that the range of the reported results for each steel was too great to be acceptable. It is evident that no cooperator obtained results consistently higher, or lower, than the others for all eight steels and, in general, the relative position of each cooperator in the columns of table 3 varies considerably from steel to steel. Consequently, the large ranges can be considered to be the result of individual experimental errors rather than of consistent differences in apparatus or procedure, and it is therefore legitimate to eliminate arbitrarily the scattered results, either high or low, in order to obtain for each steel a narrowed range that still includes the results of a majority of the cooperators.

The heavy rules in each column of table 3 inclose the acceptable values, after elimination of the scattered results. Such ranges of acceptable values would be considered satisfactory in determinations of corresponding amounts of elements such as carbon, sulphur, and manganese, for which the analytical methods are much more standardized than is the case for the determination of oxygen. It is evident that scattered values, both high and low, were discarded for all the steels except steel 2. For this steel only low results were eliminated as it was considered improbable that any cooperator would obtain too high a result for oxygen in a steel which contained more than 1 percent of manganese. In the opinion of the reviewing committee the "best" value for the oxygen content of each steel, according to the vacuum-fusion method of analysis, is approximately the mean of the acceptable values, except for steel 2. For this steel the "best" value is probably at or near the top of the acceptable range.

Each of the acceptable ranges in table 3 includes a majority of the reported values for one of the steels, but the personnel of the acceptable majority varies from steel to steel. Consideration of the details of apparatus and procedure of the individual cooperators furnishes plausible explanations for many of these deviations from acceptable results. Some of these details, compiled from the reports of the cooperators and the published references cited in table 2, are shown in table 4.

From the fact that four cooperators, 8, 18, 20, and 29, obtained results lying within the acceptable range for each of the eight steels, it is evident that acceptable results can be obtained in spite of considerable variation in apparatus and procedure. Cooperator 20 used a graphite-spiral furnace; the other three used high-frequency induction furnaces. Operating temperatures ranged from 1,550° C for cooperator 18, to 1,900° C for cooperator 20. The type of crucible support, thermal insulation of the crucible, weight of sample, and the

TABLE 4.—*Details of vacuum-fusion procedures*

Cooperator	Furnace	Operating temperature	Crucible support	Thermal insulator	Blank correction		Sample weight	Number of samples in a crucible	Surface of melt	Average time of run	Gas analysis	Remarks
					ml CO/hr	Oxygen [a]						
		°C				*Percent*	g			Min.		
6	High-frequency induction.	1,650	Pedestal	Sillimanite	<0.08	<0.00015	15	6	Open		Low pressure, gravimetric.	
8	do	1,650	Graphite-MgO	Graphite	<.2	<.0002	15	1 to 2	Graphite float	15	Low pressure, volumetric.	
11	do	1,650	Quartz	Molybdenum	.056 to .08	<.0002	8	5	Funnel top	15	Atmospheric pressure.	
14	do	[b]1,600	BeO	Alundum	.2 to 3.1	.0003 to .008	14 to 27		Graphite sleeve		Selective freezing	
15	do	1,600	Pedestal	None				1	Open		Atmospheric pressure.	100 g of Fe in crucible.
18	do	1,550	do	Water-cooled tube.	.06	<.0002	[c]35		Graphite filter and valve.	25	Atmospheric pressure (Oberhoffer).	
20	Graphite spiral	1,900			.6	.001	20	3		30	do	Low-Mn Fe in crucible.
21	do	1,750			.16 to .2	<.001	7			30	Atmospheric pressure (Meyer and Castro).	
23	High-frequency induction.	[b]1,700	Pedestal	None	3.3	.008	10	Several	Open	20	Selective freezing	
24	do	1,570	Zirconia	Sillimanite	0.77	.0033	[c]11	1		[e]150	Atmospheric pressure.	Melts sample with tin.
27	Graphite-spiral	1,700			.08 to .2	<.0003	[d]15	Several	Open	20	do	9 radiation screens.
28	High-frequency induction.	1,650	Graphite-BeO	Graphite				5	Graphite guide tube.	15	Low pressure, volumetric.	
29	do	1,650	do	do	.3 to .8	<.001	15	1 to 5	do	15	do	
31	do	1,550	Pedestal [b]	Water-cooled tube.	.014 to .05	<.0001	[f]15	Several	Graphite valve	20	Atmospheric pressure.	
34	Graphite spiral											

[a] Cooperators 14 and 23 introduced the sample into a cooled crucible and subsequently raised the temperature to the indicated operating temperature. Other cooperators introduced samples at the indicated temperatures.
[b] Cooperator 31 surrounded the lower portions of the pedestal with powdered graphite.
[c] Based on weight of sample used and time of a determination.
[d] Semidisks.
[e] 1-inch rods were forged to about 1 cm diameter to provide sample material.
[f] Samples not representative of complete cross sections of the 1-inch rods.
[g] Total time for determination of FeO, MnO, SiO_2, and Al_2O_3 fractions.

method employed for analysis of the evolved gases, varied considerably in these four procedures. Three of the four employed large furnace connections and four-stage, high-capacity diffusion pumps for rapid evacuation of the evolved gases from the furnace chamber, whereas cooperator 8 obtained acceptable results with a two-stage pump and somewhat constricted furnace connections. Protection of the quartz furnace tube by an external water-jacket instead of internal radiation screens, yielded acceptable results for cooperator 18, although it is interesting to note that Thanheiser and Brauns [3] recently reported that the interference of manganese, leading to low recoveries of oxygen, was more severe when the furnace tube was water-jacketed than when it was less drastically cooled by means of a coil of copper tubing.

The four procedures that yielded acceptable results for all eight steels have the following characteristics in common (1) a low blank correction for the apparatus; (2) precautions against interference by manganese; and (3) precautions against spattering of the molten sample. The importance of these three characteristics, common to all four of these procedures, deserves emphasis. A low blank correction, equivalent to not more than 0.001 percent of oxygen in a determination, is a prerequisite of satisfactory operation; larger or variable blank corrections are unsatisfactory for the determination of small amounts of oxygen.

It is the opinion of the reviewing committee that the presence of manganese in the sample causes some degree of interference in many of the procedures employed in this cooperative analysis because of absorption of gas by manganese vapor or sublimate. Cooperator 20 remarked that "the oxygen values for the two manganese-rich samples, 2 and 3, are perhaps somewhat low, in spite of our precautions."

Spattering as a result of gas evolution from the sample during melting or shortly thereafter may result in either high or low values for oxygen. If the spattered globules of molten metal come in contact with refractory oxides of the radiation screen or quartz furnace tube, a reaction resulting in the formation of CO may occur and cause a high value for oxygen. On the other hand, if the portion thrown out from the crucible falls to the cold bottom of the furnace tube, the oxygen of that portion of the sample is lost. The apparatus of each of the four cooperators, who obtained consistently satisfactory results, was arranged to prevent loss of molten spatters or their contact with hot refractory oxides. Cooperator 8 used a graphite float and cooperator 18 a graphite filter to prevent the spattered material from leaving the crucible; cooperator 20 apparently used a deep crucible covered with a graphite funnel in a graphite-spiral furnace that did not contain any refractory oxides. In the apparatus of cooperator 29, a thin-walled graphite tube extended from the top of the crucible to the bottom of the guide tube through which the

[3] Arch. Eisenhüttenw. **9**, 435 (1935-36).

samples were dropped. With this arrangement, any spattered particles struck the inner surface of the graphite tube and dropped back into the crucible. Only rarely would a spattered particle be evolved with sufficient velocity to reach the guide tube.

Spattering is probably one of the principal causes for the erratic results of individual determinations and for the divergence between the results of different cooperators. It is significant that the greatest divergence of reported results is for open-hearth iron 7, which has the largest oxygen content and consequently the greatest tendency to spatter. The results for steel 3, although less divergent than the results for iron 7, are more divergent than those of other steels of similar oxygen content. However, steel 3 is relatively high in nitrogen and the total volume of gases evolved is appreciably greater than that from other steels of similar oxygen content. Consequently the divergence of results for steel 3 also may be ascribed, in part, to spattering. It has been previously mentioned that gradual melting of the sample is sometimes employed to reduce the tendency to spatter, but this procedure apparently increases the susceptibility to manganese interference.

The fractional vacuum-fusion procedure, which is currently a subject of considerable interest, is represented in these data by the results of only one cooperator, 24, whose values for total oxygen are usually within the acceptable ranges but slightly high for steels 3, 4, and 5. Comparison of the values obtained for the separate fractions with the results of residue methods is given in a later section.

The reports of the other cooperators who used the vacuum-fusion procedure comprise 80 values, of which 47 are within the acceptable ranges, 14 are high, and 19 are low. In several instances it is possible to account for high or low results on the basis of one or more of the following sources of error (1) spattering; (2) interference by manganese; (3) high or irregular blank correction; (4) slow melting; (5) improper sampling; and (6) miscellaneous causes.

(a) RECOMMENDATIONS FOR THE DETERMINATION OF OXYGEN BY THE VACUUM-FUSION METHOD

(1) *Furnace construction.*—Either a high-frequency induction furnace or a graphite-spiral resistor may be used. The presence of refractory oxides in the furnace chamber is undesirable, particularly if they are hot or in contact with hot graphite; beryllium oxide appears to be least objectionable.

(2) *Analysis of the evolved gases.*—The selection of a procedure and apparatus for the analysis of the gases evolved from the sample is apparently a matter of personal preference. The determination may be made volumetrically or gravimetrically, at low pressure or at atmospheric pressure, or by selective freezing.

(3) *Procedure.*—Complete reduction of the oxides in these steels can be obtained in a reasonable time at temperatures as low as 1,550° C.

Preliminary "outgassing" of the furnace is accomplished at a temperature about 200° C higher than the operating temperature. The pressure in the furnace at operating temperature should not exceed 0.001 mm of Hg at the beginning of a determination. The blank correction for the apparatus should not exceed 0.001 percent of oxygen in a determination. The size of the sample depends upon the storage capacity of the apparatus and on the oxygen content of the material, but the sample must be representative. Spattering of the melting sample or of the molten bath should be prevented, but a satisfactorily reliable and convenient means of accomplishing this end has not yet been developed. The evolved gases should be removed rapidly and completely from the furnace chamber to avoid secondary reactions with the walls and contents of the furnace; a four-stage, mercury-diffusion pump of high capacity is frequently employed. Constricted or relatively long connections between the furnace and the diffusion pump should be avoided.

(4) *Manganese interference.*—The presence of 0.5 percent or more of manganese in a steel to be analyzed constitutes a potential source of error in the apparatus generally used, either as a result of the presence of manganese as vapor in the furnace chamber or condensed on the furnace walls, or both. Established precautions to minimize the error from this source include (a) the rapid and complete removal of evolved gases from the furnace chamber; (b) the use of a fresh crucible for each determination or dilution of the sample with manganese-free iron; and (c) frequent cleaning of the furnace chamber. The minimum manganese content that will produce a noticeable error apparently varies with the construction of the apparatus and with the procedure. Two of the cooperators, 27 and 31, believe that their procedures are free from error by interference from manganese contents up to 3 and 12 percent, respectively. Unpublished results of experiments on steel 2 at the National Bureau of Standards showed that two and sometimes three consecutive samples could be melted in the same crucible without appreciable error from manganese interference, provided that a high-capacity pump was used. On the other hand, when a pump of lower capacity was used, with somewhat higher furnace pressure, error from this source was noticeable in the second determination. It was also found that the determination of oxygen in steel 2 was affected somewhat by the size of the sample, slightly higher values being obtained from the smaller samples. A possible explanation is that they melted more rapidly and the gas evolution was completed before appreciable evolution of manganese vapor occurred. This appears to be additional evidence of the usefulness of rapid melting of the sample for minimizing the error from interference by manganese.

(b) DETERMINATIONS OF NITROGEN AND HYDROGEN

Several cooperators reported results for nitrogen and hydrogen, as well as for oxygen. These are summarized in tables 5 and 6. The

results of different cooperators for nitrogen are in quite satisfactory agreement, allowance being made for an occasional high or low result. The good agreement of the single set of results by the solution-distillation method with those obtained by vacuum fusion indicates that both methods are dependable in determining the nitrogen content of these steels.

The results of the four cooperators who determined hydrogen by the vacuum-fusion method indicate that the hydrogen content for each of the eight steels is less than 0.001 percent.

The desirability of accurate determinations of amounts of hydrogen considerably less than 0.001 percent by weight is indicated by recently reported results. Thanheiser [4] reported that significant differences in the elongation and reduction of area of samples of freshly rolled rail steel occurred when the hydrogen content was reduced from 2 or 3 cc per 100 g to lesser amounts by means of annealing and aging treatments. These figures indicate that a hydrogen content of 0.0002 percent, by weight, may affect the properties of steel to an appreciable extent, and that even smaller amounts may be significant. The accurate determination of such amounts of any element is indeed a problem.

TABLE 5.—*Determination of nitrogen*
(Percent)

Cooperator	STEELS							
	1	2	3	4	5	6	7	8
VACUUM-FUSION METHOD								
8	0.0025	0.0044	0.015	0.005	0.004	0.005	0.0045	0.004
11	.0024	.0024	.014	.0046	.004	.004	.003	.003
14	.0019	.0038	.011	.0035	.003	.0035	.0055	.0035
18	.003	.005	.010	.0088	.006	.005	.008	.005
24	.003	.003	.015	.002	.002	.003	.004	.0025
29	.003	.005	.016	.006	.005	.006	.005	.005
SOLUTION-DISTILLATION METHOD								
2	.003	.006	.016	.005	.004	.005	.005	.004

TABLE 6.—*Determination of hydrogen*
(Percent)

Cooperator	STEELS							
	1	2	3	4	5	6	7	8
11	0.00014	0.00016	0.00013	0.00007	0.00009	0.00007	0.00054	0.00017
18	.0001	.0001	.0001	.0001	.00005	.00004	.0003	.0003
24	.0006	.0008	.0006	.0003	.0005	.0003	.0001	.0003
29	.00002	.00009	.0002	.0002	.0002	.0003	.0004	.0015

2. IODINE METHOD

In the iodine method for determining oxides in steel, the sample is treated with a suitable solution of iodine. Iron, silicon, and manganese are dissolved, and a residue of carbonaceous material (carbides in certain cases) and unattacked oxides remains.

[4] Stahl u. Eisen 56, 1125 (1936).

In the procedure described by Cunningham and Price (table 2, cooperator 13), a 5- to 10-g sample is treated at 3 to 5° C in a stoppered flask with an aqueous solution of iodine in ferrous iodide.[5] By the method of Rooney and Stapleton (table 2, cooperator 31) the sample is treated with a solution of iodine in anhydrous methyl alcohol (70 g of iodine in 600 ml of alcohol). Rather elaborate precautions are necessary to exclude all moisture and oxygen from the solvent and containers while the steel is dissolving and during filtration of the resulting solution. Willems (table 2, cooperator 10) recommended the use of a solution of iodine in absolute ethyl alcohol and filtration through an ultrafilter.

The proponents of the alcoholic iodine solutions claim that higher recoveries of oxides of iron and manganese are obtained with these solvents than with aqueous solutions of iodine in ferrous and potassium iodide.

The values for Al_2O_3, SiO_2, MnO, and FeO, obtained by the cooperators, are given in tables 7, 8, 9, and 10.[6] Reports were submitted by 12 cooperators though not all reported values for all of the 8 steels. Eight cooperators used an aqueous iodine solvent, essentially the procedure described by Cunningham and Price; three used a solution of iodine in anhydrous methyl alcohol, as described by Rooney and Stapleton, and one employed a solution of iodine in absolute alcohol, as described by Willems. Some of the values reported by cooperator 31 were obtained by a variant of Rooney and Stapleton's method, but details of the modified procedure are not yet available.

[5] Prepared as follows: To 5 g of plain-carbon steel drillings in a 300-ml Erlenmeyer flask are added 25 ml of water, 4 g of ammonium citrate, and 30 g of iodine. The flask is shaken for several minutes in ice water and then 30 g of additional iodine is added. The shaking is continued until all the iodine has dissolved, whereupon the solution is filtered. The total volume of the filtrate and washings should not exceed 75 ml and this amount of solution is sufficient for a 5-g sample. For larger samples, proportionally more solvent is used.

[6] Total Al, Si, Mn, and Fe in the insoluble residues are reported as the single oxides, which may exist in the steel as such, or in combination as silicates or spinels.

TABLE 7.—*Determinations of* Al_2O_3 *by the iodine method*

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Iron 7		Steel 8	
Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator
CUNNINGHAM AND PRICE PROCEDURE															
0.010	9	0.039	9	0.021	9	0.025	9	0.016	9	0.038	9	0.020	9	0.032	29
.005	30	.004	30	.006	16	.011	21	.002	21	.005	7	.018	21	.028	9
.003	21	.003	21	.005	21	.007	7	.002	29	.003	21	.014	16	.027	7
.002	19	.002	29	.003	30	.0055	29	.000	7	.002	30	.004	19	.025	30
.0003	29	.001	19	.002	19	.004	16	•.000	16	•.000	16	.0015	29	.017	21
.000	7	.000	7	.000	7	.003	30	.000	30	----------	----------	.000	7	.016	16
•.000	16	•.000	16	.000	29	.0025	19	----------	----------	----------	----------	.000	30	.012	19
SELECTED VALUES															
0.002 ±.002		0.002 ±.002		0.002 ±.002		0.006 ±.002		0.002 ±.002		0.002 ±.002		0.002 ±.002		0.030 ±.003	
ROONEY AND STAPLETON PROCEDURE															
0.006	31	0.014	31	0.021	27	0.008	27	0.0035	22	0.0042	22	0.022	27	0.037	31
.004	22	.0065	22	.0075	22	.0065	31	.0025	31	.0025	31	.013	31	.033	22
.002	27	.003	27	.005	31	.005	22	.001	27	.001	27	.012	22	.031	27
WILLEM'S METHOD															
•0.000	10	•0.000	10	0.010	10	•0.000	10	0.003	10	•0.000	10	0.005	10	0.020	10

• Reported by dash. It is assumed that a determination was made and no detectable amount found.

TABLE 8.—*Determinations of* SiO_2 *by the iodine method*

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Iron 7		Steel 8	
Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator
CUNNINGHAM AND PRICE PROCEDURE															
0.018	9	0.041	9	0.037	9	0.015	9	0.049	9	0.049	9	0.012	9	0.040	9
.005	30	.012	21	.012	30	.015	30	.020	30	.014	30	.011	30	.010	30
.005	16	.012	30	.007	19	.008	16	.019	16	.010	13	.004	21	.005	16
.005	21	.010	16	.006	7	.004	21	.015	13	.009	16	.002	16	.0025	7
.0022	29	.006	29	.005	13	.002	7	.015	29	.008	21	.002	19	.002	21
.0015	13	.006	7	.005	29	.0018	13	.013	7	.006	7	.0013	29	.002	19
.000	7	.006	13	.004	21	.0012	29	.012	21	----------	----------	.000	7	.0007	29
----------	----------	----------	----------	.003	16	.0005	19	----------	----------	----------	----------	•.000	13	•.000	13
SELECTED VALUES															
0.003 ±.002		0.009 ±.003		0.005 ±.002		0.002 ±.002		0.016 ±.003		0.009 ±.003		0.002 ±.002		0.003 ±.002	
ROONEY AND STAPLETON PROCEDURE															
0.0034	22	0.027	22	0.017	31	0.0037	27	0.021	27	0.011	22	0.0013	22	0.0055	27
.0027	27	.025	31	.014	22	.0016	22	.017	22	.011	31	.001	31	.0029	31
.0017	31	.0091	27	.0015	27	.0013	31	.016	31	.009	27	.0009	27	.0026	22
WILLEM'S METHOD															
•0.000	10	0.012	10	0.012	10	0.015	10	0.007	10	•0.000	10	•0.000	10	0.006	10

• Reported by dash.

TABLE 9.—*Determinations of* MnO *by the iodine method*

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Iron 7		Steel 8	
Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator
CUNNINGHAM AND PRICE PROCEDURE															
0.013	30	0.029	9	0.025	9	0.007	30	0.010	9	0.015	9	0.030	13	0.006	30
.003	21	.007	30	.021	16	.0065	9	.009	30	.011	16	.030	7	.005	9
.0025	9	.005	16	.013	21	.006	16	.007	16	.011	30	.027	19	.0035	16
.002	7	.005	21	.012	30	.002	13	.006	21	.007	21	.026	9	.002	7
.002	16	.0025	13	.009	13	.0003	29	.003	7	.005	13	.022	21	.002	21
.002	29	.0025	29	.008	29	.000	7	.002	29	.004	7	.021	29	.0015	29
.0015	13	.002	7	.0055	7	.000	21	.002	13	----------	----------	.021	30	.001	13
----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	.018	16	----------	----------
SELECTED VALUES															
0.002±.002		0.004±.002		0.012±.004		0.002±.002		0.004±.002		0.008±.003		0.025±.005		0.003±.002	
ROONEY AND STAPLETON PROCEDURE															
0.055	31	0.041	27	0.141	22	0.0061	31	0.011	31	0.012	31	0.027	31	0.025	27
.044	22	.036	22	.120	31	.0057	22	.009	22	.011	22	.023	22	.0075	22
.000*	27	.032	31	.016	27	*.000	27	.005	27	.002	27	.019	27	.0071	31
WILLEM'S METHOD															
0.008	10	0.0055	10	0.205	10	*0.000	10	0.005	10	0.029	10	0.069	10	0.0026	10

* Reported by dash.

TABLE 10.—*Determinations of* FeO *by the iodine method*

TABLE 10.—*Determinations of* FeO *by the iodine method*

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Iron 7		Steel 8	
Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator
CUNNINGHAM AND PRICE PROCEDURE															
0.015	30	0.024	16	0.015	13	0.018	30	0.014	30	0.021	9	0.43	16	0.018	13
.014	16	.023	13	.014	7	.014	16	.014	13	.018	16	.414	7	.017	16
.012	13	.015	30	.012	30	.011	7	.009	7	.014	7	.393	13	.014	30
.010	7	.013	7	.011	9	.0055	13	.009	16	.013	30	.39	30	.014	29
.010	21	.010	29	.007	21	.0035	9	.008	21	.013	13	.377	19	.010	21
.007	29	.008	21	.005	29	.002	29	.007	29	.007	21	.33	29	.009	7
.002	9	.0047	9	.003	16	.0006	21	.0036	9			.32	9	.0042	9
												.262	21		
SELECTED VALUES															
0.012±.004		0.013±.005		0.011±.004		0.004±.002		0.010±.004		0.010±.004		0.39±.03		0.014±.005	
ROONEY AND STAPLETON PROCEDURE															
0.063	22	0.014	22	0.026	22	0.015	31	0.025	27	0.014	31	0.481	22	0.033	22
.054	31	.0073	27	.021	31	.011	22	.012	31	.010	22	.446	31	.030	31
.004	27	.0065	31	.014	27	.006	27	.008	22	.008	27	.382	27	.005	27
WILLEM'S METHOD															
0.016	10	0.027	10	0.011	10	0.033	10	0.024	10	0.038	10	0.111	10	0.017	10

The values obtained by the iodine method vary rather widely among themselves. Undoubtedly, inaccurate chemical analysis of the insoluble residue is responsible in part. In studying the data of the eight cooperators who used an aqueous solution of iodine, it was observed that the results obtained by some were consistently high or low, and that the values obtained by cooperators 7, 13, 19, 21, and 29 were generally in good agreement. The "selected values" given in tables 7, 8, 9, and 10 were chosen by the committee from the data of those who used the aqueous solvent and were based largely on the results of the five cooperators mentioned. It is believed that these selected values are representative of results that may be expected by carefully following the Cunningham and Price procedure.

Because of the limited number of cooperators who used the alcoholic solvents and the rather wide variation in the reported results, no selected values were chosen for this group. However, a comparison of these results with the selected values for the aqueous iodine method is discussed in a later section.

In the following sections there is recorded a brief discussion of the values reported by the eight cooperators who used the aqueous iodine solvent. These cooperators used the Cunningham and Price method, except for some small changes by some of the analysts. For example, cooperator 7 used an I–FeI_2 solution containing approximately 50 g of iodine and 0.8 g of ammonium citrate per 100 ml; cooperator 19 used an I–KI solution containing 1 percent of ammonium citrate, and cooperator 29 used somewhat larger samples (18 to 20 g).

The permissible variations within the selected ranges may seem rather wide. In general, however, the spread, except for FeO, is of about the same order as obtains in the determination of other constituents present in small amounts in ferrous alloys. Furthermore, it should be noted that a difference of 0.005 percent of FeO or MnO, or 0.002 percent of Al_2O_3 or SiO_2, is equivalent to but 0.001 percent of oxygen.

Of the 53 values for the determination of Al_2O_3, received from cooperators who used an aqueous solution of iodine as the solvent, 33 are within the selected ranges (indicated by the heavy rules in the columns of tables 7, 8, 9, and 10), 14 above and 6 below. On the very low-alumina steels, the errors are usually on the high side, probably because of faulty blank corrections. On the other hand, low values were reported by a number of cooperators for high-alumina steel 8, another indication of the tendency toward inaccurate analysis of the insoluble residues. The values obtained by the Rooney and Stapleton procedure (cooperators 22, 27, and 31) are of the same order of magnitude but frequently are higher than the selected values.

For the determination of SiO_2, 59 values were received from the cooperators who used the aqueous-iodine solvent. Of these, 41 are within the selected range, 15 above and 3 below. The values obtained by following the Rooney and Stapleton procedure (cooperators 22, 27, and 31) are, in general, of the same order of magnitude as the selected values; results obtained by following Willems' procedure (cooperator 10) are within the selected ranges only for steels 2 and 7.

For the determination of MnO, 56 values were received from the group who employed the aqueous-iodine solvent, of which 40 are within the selected range, 13 above and 3 below. The values obtained by the Rooney and Stapleton procedure vary considerably, and, in

general, are higher than those obtained with the aqueous-iodine solvent. Part of this difference undoubtedly can be attributed to the fact that MnS is not as soluble in the alcoholic as in aqueous-iodine solutions, and some MnS is reported as MnO. It is noteworthy that in steel 2 the MnO values of the alcoholic group are distinctly higher than the selected value, which brings up the question of whether or not MnO can be quantitatively recovered by the aqueous solvent from a steel of the 2 type. On the other hand, the values for MnO in iron 7 by the aqueous and alcoholic methods are in good agreement. In this iron the maximum possible MnO would be 0.031 percent if the total Mn (0.024 percent) be calculated to MnO.

For the determination of FeO, 56 values were received from those who used the aqueous-iodine solvent, of which 37 are within the selected range, 8 above and 11 below. It will be noted that the variation within the selected range is greater for FeO than for the other three oxides. This condition naturally complicates the choice of a selected value. The values by the Rooney and Stapleton procedure are frequently higher than the selected values. In general, it appears as though the FeO values obtained by the iodine method are somewhat unreliable. For example, with steel 4, the selection of 0.004 percent of FeO may be questioned.

3. ACCURACY OF THE VACUUM-FUSION AND AQUEOUS-IODINE METHODS

These cooperative analyses were undertaken in the hope that the results of different operators would be in sufficiently close agreement to define the best value, or a reasonable range of values, that should be obtained by each of the analytical methods. Agreement in the results obtained by different methods, for the same steel, would establish the accuracy of the methods that were in agreement. To date this hope has not been fully realized. The outstanding feature of these data is the range of results, i. e., the lack of agreement, in the values obtained by a group of operators using the same method even when each analyst confirms his own results by duplicate or multiple determinations. The information available at present does not suffice to determine whether these discrepancies are primarily the result of inaccuracies in the methods, minor variations in apparatus and procedure of different investigators, or the personal equation.

A selection of representative ranges or "best" values has been possible only for the vacuum-fusion and aqueous-iodine methods as previously described. None of the other methods of analysis are represented by enough concordant results to indicate "best" values, and even in some of the data of the vacuum-fusion and aqueous-iodine methods there is sufficient lack of concordance to render the selection of "best" values difficult and somewhat uncertain. The determination of FeO by the iodine method is a particular illustration of this point.

Direct comparison of the "best" values by the vacuum-fusion and aqueous-iodine methods can be made on the basis of the total oxygen content. This is given directly by the results of the vacuum-fusion analyses and can be computed in the iodine method from the selected values for Al_2O_3, SiO_2, MnO, and FeO on the assumption that other combinations of oxygen are not present. This assumption is not

strictly correct; the presence of small amounts of other oxides was detected [7] by some of the cooperators, but the amount of oxygen combined in these other oxides may be neglected for present purposes.

Values for total oxygen by the two methods are shown in table 11. Entirely satisfactory agreement, well within the permissible limits of error for such determinations, is evident for steels 4, 5, 6, and 8. Such duplication of results by two independent methods is good evidence of the accuracy of both methods, as applied to these four steels, all of the "killed" type. Steels 4 and 8 were killed with aluminum, steels 5 and 6 with silicon. The iodine method is expected to give its most accurate results on steels of this type, in which the oxygen is present principally as Al_2O_3 and SiO_2. The good agreement of the results by the two methods is evidence that appreciable amounts of Al_2O_3 and SiO_2 do not interfere with the satisfactory operation of the vacuum-fusion method.

TABLE 11.—*Comparison of results by the vacuum-fusion and aqueous-iodine methods*

Steel	Selected values for total oxygen		Steel	Selected values for total oxygen	
	Vacuum-fusion method [a]	Aqueous-iodine method [b]		Vacuum-fusion method [a]	Aqueous-iodine method [b]
	Percent	*Percent*		*Percent*	*Percent*
1	0.018	0.006	5	0.009	0.013
2	.017	.010	6	.007	.010
3	.017	.009	7	.106	.095
4	.002	.005	8	.017	.020

[a] Selected values from vacuum-fusion determinations.
[b] Computed from results for Al_2O_3, SiO_2, MnO, and FeO obtained by the aqueous-iodine method.

Steel 2, a silicon-killed steel, with a manganese content of 1.15 percent, gave a "best" value for total oxygen by the iodine method only half as great as the "best" value by the vacuum-fusion method. In view of the established fact that the presence of manganese frequently causes low recoveries of oxygen to be obtained, the results of the vacuum-fusion method should not be considered as being too high. It is more probable that the iodine results are low, perhaps because the silicates in this steel are different in composition and more soluble than those in steels 4, 5, 6, and 8. Microscopic studies (cooperators 1, 26, and 33) indicated that the silicate inclusions are larger and more numerous in steel 2 than in steels 5 and 6; in steels 4 and 8 the inclusions are chiefly Al_2O_3.

For steels of the "rimming" type, 1, 3, and 7, the total oxygen by the vacuum-fusion method was appreciably higher than by the iodine method.[8] On the assumption that the vacuum-fusion method yields correct results for killed steels, containing the difficultly reducible oxides, Al_2O_3 and SiO_2, it is reasonable to conclude that this method should yield correct results for rimming steels in which the easily reducible oxides, FeO and MnO, are predominant. It is believed,

[7] Cooperator 7 reported 0.0013 percent of Cr_2O_3 in steel 2, and 0.010 percent of Cr_2O_3 in iron 7; cooperator 29 reported 0.0015 percent of Cr_2O_3 in steel 2, 0.007 percent of Cr_2O_3 and some Fe_2O_3 in iron 7, and 0.004 percent of P_2O_5 in steel 3; cooperator 22 reported 0.0026 percent of TiO_2 in steel 2; cooperator 31 reported 0.0034 percent of TiO_2 in steel 2 and Cr_2O_3 in four of the steels as follows: 0.0012 percent in steel 1; 0.0014 percent in steel 2; 0.0077 percent in iron 7; and 0.0006 percent in steel 8.

[8] This statement is based on the actual difference and not on the percentage difference in results by the two methods. In the latter respect the two methods are in fairly good agreement for iron 7.

therefore, that the results obtained by vacuum-fusion for steels 1, 3, and 7 are approximately correct, and, on the other hand, that the results by the iodine method are somewhat low, perhaps on account of analytical difficulty in determining FeO and MnO by this method or because of difficulty in the selection of the best values from the reported data for FeO and MnO. It is not fully apparent why the greatest difference in results by the two methods was obtained for steel 1, unless it is because the MnO in this steel is not combined with SiO_2 and is therefore more readily dissolved than in the other steels.

The evidence of the available data in regard to the accuracy of the two methods may be summarized as follows:

The accuracy of the vacuum-fusion method for silicon-killed and for aluminum-killed steels (4, 5, 6, and 8) is demonstrated by agreement with the results of the aqueous-iodine method. The accuracy obtained for killed steels justifies the assumption of accuracy for unkilled steels. A reasonable value was obtained for the oxygen content of steel 2 and indicates that the presence of 1.15 percent of manganese in a steel does not introduce serious error in the best results obtainable by the vacuum-fusion method.

The accuracy of the iodine method for aluminum-killed steels and for some silicon-killed steels is demonstrated by agreement with the results of the vacuum-fusion method, for steels 4, 5, 6, and 8. The low results obtained for steel 2 indicate that inaccurate results may be obtained on some silicon-killed steels. Low results were obtained on rimming steels. Satisfactory concordance in the results obtained by the iodine method, particularly for FeO, is not yet attainable.

4. HYDROGEN-REDUCTION METHOD

This method depends upon the reduction of oxides in the sample by means of purified hydrogen at elevated temperatures. The amount of water vapor in the hydrogen leaving the furnace indicates the amount of oxides reduced. It is generally believed that FeO and MnO are completely reduced under these conditions, but that refractory compounds such as Al_2O_3 and certain silicates are reduced only partially or not at all.

Four of the cooperators in this project reported results obtained by this method. Essential details of apparatus and procedure, which differed considerably for the four, have been published elsewhere.[9]

The data reported by these four cooperators and shown in table 12, are too few and the concordance of results is not sufficiently close to permit a selection of representative values for the hydrogen-reduction method. For each steel the four values extend over a considerable range, frequently greater than that of the 15 determinations by the vacuum-fusion method.

[9] Metals Tech. (December 1936).

TABLE 12.—*Determinations of oxygen by hydrogen-reduction methods.*

STEEL

1		2		3		4		5		6		7		8	
Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator	Percent	Cooperator
0.024	2	0.027	2	0.027	2	0.012	5	0.022	2	0.010	2	0.106	5	0.023	[illegible]
.021	32	.020	5	.025	5	.008	2	.016	5	.010	5	.100	32	.020	[illegible]
.020	5	.012	32	.021	32	.0077	17	.0078	32	.0043	32	.098	17	.015	[illegible]
.019	17	.0077	17	.018	17	.0005	32	.0013	17	.0028	17	.076	2	.0028	17

A comparison of the hydrogen-reduction results with the acceptable values for the vacuum-fusion method (see table 3) shows that the results of only one cooperator (32) are consistently near to or within the limits of acceptable values established by the vacuum-fusion method. The available information is not sufficient to account for the lack of agreement between the results of different investigators or between the results by the hydrogen-reduction and vacuum-fusion methods. The hydrogen-reduction method is generally assumed to recover only the oxygen combined as FeO or MnO, but for steel 8, in which the oxygen is present chiefly as Al_2O_3, three of the four results are as high as the results by the vacuum-fusion method. On the other hand, for the sample of open-hearth iron in which the oxygen is present chiefly as FeO and MnO, the results tend to run lower than those by vacuum-fusion. It is of interest to note that the best agreement within the results by the hydrogen-reduction method is obtained for steel 1, and for this steel the results by hydrogen-reduction and vacuum-fusion are in good agreement, whereas those by iodine and vacuum-fusion are not. More data, and particularly more concordant data, are needed to establish the accurancy of the hydrogen-reduction method.

5. ELECTROLYTIC METHOD

By making the sample the anode in an electrolytic cell with a suitable electrolyte, and by controlling the conditions of electrolysis, the soluble metallic constituents can be separated from the insoluble nonmetallic material. After electrolysis, the loss in weight of the anode is determined and the insoluble residue is collected and analyzed. The four following electrolytes were used by the seven cooperators reporting results by this method:

(a) An aqueous solution containing 3 percent of $FeSO_4.7H_2O$ and 1 percent of NaCl, as recommended by G. R. Fitterer and coworkers, MnO, SiO_2, and Al_2O_3 being determined in the insoluble residues. Values for FeO cannot be obtained since basic ferric sulphate and ferrous hydroxide precipitate during electrolysis and contaminate the residue.

(b) An aqueous solution containing approximately 45 g of magnesium iodide and 2 g of iodine per liter, as recommended by F. W. Scott for the determination of FeO, MnO, Al_2O_3, and SiO_2, the claim being made that iron dissolves without hydrolysis in this electrolyte, and that any sulphides, phosphides, and carbides in steel are completely decomposed.

(c) A 3-percent aqueous solution of ferrous chloride, recommended by H. Styri for determining SiO_2 and Al_2O_3. In some experiments a solution containing 3 percent of sodium citrate and 0.1 percent of ferrous chloride was used in the anode compartment.

(d) A 0.1*N* potassium bromide solution containing about 10 percent of sodium citrate, for the anode compartment and a 10-percent solution of a copper salt, either sulphate or bromide for the cathode compartment, as recommended by Benedicks, whose published description stated that the determination of FeO, Al_2O_3, and SiO_2 was adequate but that the determination of MnO was not quite satisfactory. This was used for determining the four constituents listed.

The results reported by seven cooperators are shown in table 13. Two cooperators heat treated the samples before electrolysis to see if heat treatment and the resulting redistribution of carbides affected the determination of Al_2O_3 and SiO_2.

The comparison of results obtained by different observers using the same electrolyte is frequently complicated by variations in methods of analysis and other departures from uniform procedure. There are not enough data available to justify the selection of "best" values for any one electrolyte or for the electrolytic procedure, in general. However, the results obtained by electrolytic methods can be compared with the selected values by the aqueous-iodine method, shown at the bottom of each section of table 13.

Electrolytic methods, in general, are believed to be more reliable for determinations of SiO_2 and Al_2O_3 than for FeO and MnO. The latter determinations are complicated by the presence of carbides and sulphides in the insoluble residue; by the presence of hydrated compounds formed by anodic oxidation during electrolysis; and by the presence of small metallic particles from mechanical disintegration of the anode. The consistently high results for FeO and MnO, by electrolytic methods, as compared with the selected values by the aqueous-iodine method, may reflect the analytical difficulties in the determination of FeO and MnO, rather than a consistent difference in the two methods in separating FeO and MnO from the rest of the sample. The values by the iodine method are believed to be approximately correct for steels 4, 5, 6, and 8, but they are low for steels 1, 2, 3, and 7. Consequently, if the electrolytic determinations of FeO and MnO are accurate, they should coincide with the iodine results for steels 4, 5, 6, and 8 and should be higher than the iodine results for steels 1, 2, 3, and 7. This is not the case; the electrolytic values are scatteringly higher than those by the iodine method by about the same amount for each steel.

There is somewhat better agreement between results, by the two methods, for SiO_2 and Al_2O_3. However, even in these determinations there is a decided lack of concordance in results obtained by electrolytic methods.

TABLE 13.—*Results obtained by electrolytic methods*

Method	Cooperator	STEEL 1	2	3	4	5	6	7	8
DETERMINATIONS OF Al_2O_3(%)									
Fitterer	3	0.002	0.009	0.004	0.025	0.002	0.002	0.006	0.016
	*3H	nil	.002	.003	.024	.002	.004	.005	.024
	30	.0007	.0007	.0003	.003	.001	.002	.0004	.018
Scott	4	.004	nil	nil	.006	nil	nil	.004	.035
	20	.004	----	----	.009	.005	.007	.010	.042
	35	.002	.004	.003	.006	.002	.003	.003	.031
Styri	12	.001	.005	.002	.032	.0015	.003	.003	.021
	†12H	.0015	.004	.003	.022	.002	.003	.003	.025
Benedicks	20	.005	.013	.006	.012	.006	.009	.009	.070
Best values from aqueous-iodine method	----	0.002±.002	0.002±.002	0.002±.002	0.006±.002	0.002±.002	0.002±.002	0.002±.002	0.030±.003
DETERMINATIONS OF SiO_2 (%)									
Fitterer	3	0.005	0.070	0.008	0.006	0.024	0.081	0.006	0.006
	*3H	.011	*.054	.010	.004	.017	.014	.004	.007
	19	.004	.021	.020	.002	.016	.018	.002	.003
	30	.001	.014	.0045	.001	.027	.042	.0015	.0015
Scott	4	.001	.010	.003	.0004	.013	.007	.0008	.004
	20	.003	----	----	.004	.024	.013	.009	.010
	35	.002	.013	.0035	.004	.016	.009	.0015	.003
Styri	12	.003	.047	.004	.0045	.0055	.046	.004	.004
	†12H	----	.051	----	.0065	----	.07	----	.007
Benedicks	20	.020	.079	.027	.024	.076	.140	.092	.013
Best values from aqueous-iodine method	----	0.003±.002	0.009±.003	0.005±.002	0.002±.002	0.016±.003	0.009±.003	0.002±.002	0.003±.002

DETERMINATIONS OF MnO (%)

DETERMINATIONS OF MnO (%)

Fitterer	3	[d]—0.001	nil	[d]—0.021	0.012	0.009	0.079	0.028	0.103
	[a] 3H	.014	0.017	.080	.017	.019	.041	.018	.030
	19	.029	.097	.041	.030	.053	----------	.019	.055
	30	.018	.102	.055	.083	.049	.051	nil	.052
Scott	4	.006	.033	.082	.007	.007	.0035	.0235	.009
	20	[c].001	[c].001	[c].004	[c].001	[c].002	[c].001	[c].022	[c].004
	35	.002	.009	.011	.004	.008	.009	.025	.011
Benedicks	20	[c].013	[c].073	[c].184	[c].008	[c].014	[c].016	[c].019	[c].023
Best values from aqueous-iodine method	----------	0.002±.002	0.004±.002	0.012±.004	0.002±.002	0.004±.002	0.008±.003	0.025±.005	0.003±.002

DETERMINATIONS OF FeO (%)

Scott	4	0.020	0.009	0.005	0.012	0.015	0.008	0.421	0.004
	20	[c].185	[c].016	[c].515	[c].080	[c].052	[c].094	[c].480	[c].195
	35	.015	.009	.012	.008	.008	.011	.342	.010
Benedicks	20	[c].091	[c].073	[c].047	[c].040	[c].040	[c].029	[c].347	[c].220
Best values from aqueous-iodine method	----------	0.012±.004	0.013±.005	0.011±.004	0.004±.002	0.010±.004	0.010±.004	0.39 ±.03	0.014±.005

[a] Cooperator 3 determined Al_2O_3, SiO_2, and MnO in samples as received (3) and after heat treatment (3H). For determinations of SiO_2 the samples were annealed for 18 hours at 650° C; for MnO the samples were held at 1,000° C for ½ hour and quenched in water.

[b] Cooperator 12 determined Al_2O_3 in "soft" samples as received (12) and in "hard" samples quenched from 1,100° C in saturated brine (12H).

[c] After a second annealing of steel 2 at 675° C for 18 hours, the value obtained for SiO_2 was 0.018 percent.

[d] Negative values for MnO indicate discrepancies in the separation of MnO and MnS.

[e] Including sulphides.

The best agreement with the selected values for the iodine method was obtained with Scott's electrolyte (cooperators 4 and 35). The procedure was varied, however, from the published description (table 2, cooperator 4), particularly in the treatment of the residue to remove sulphides, iron salts, and metallic particles prior to analysis. In one modified method (cooperator 4) the residue was washed with KI solution, then with a 12-percent solution of $CuSO_4.5H_2O$ (previously neutralized with MgO), filtered, and the residue digested with 25-percent sodium citrate solution. It was then filtered, washed with 2-percent ammonium citrate solution and, thereafter, treated as described in the published article. In the other modified procedure (cooperator 35) the electrolysis was conducted at constant voltage (about 2 volts) and in a neutral atmosphere and, without removal from the neutral atmosphere, the residue was washed with 5-percent sodium citrate and then with copper sulphate solution. It was rewashed with these reagents and then with hot 5-percent NaOH solution and finally with water.

The results obtained by these two procedures are in excellent agreement in practically all of the determinations. The values for Al_2O_3 and SiO_2 are invariably within or very near the range of the aqueous-iodine values; the results for MnO and FeO are in good agreement with those of the iodine method, except for high results in one case (cooperator 4) in the determination of MnO in steels 2 and 3. Other results obtained with Scott's electrolyte for SiO_2 and Al_2O_3 (cooperator 20) sometimes are higher than, but, in general, in good agreement with the above. It was suggested however (cooperator 20) that the results obtained for SiO_2 may be somewhat high on account of solubility of glass during the prolonged electrolysis, and it was also stated that the sulphides and phosphides of manganese were strongly decomposed but the corresponding compounds of iron only partially in Scott's electrolyte. Furthermore, the residue was observed often to contain appreciable amounts of fine-grained, undecomposed metallic ingredients. The combined effect of these factors, according to cooperator 20, was to yield erroneously high results for FeO and, to a less pronounced extent, for MnO. Comparison with the selected values by the aqueous-iodine method indicates that the error due to these factors is appreciable only in the determination of FeO; comparison with the values obtained by the modified procedures (cooperators 4 and 35) indicates that the error even in the determination of FeO can be largely eliminated by a suitable purification treatment of the initial residue.

Comparison of results obtained with Benedicks' and with Scott's electrolyte by the same analyst (cooperator 20) shows that consistently higher results for Al_2O_3 and decidedly higher results for SiO_2 were obtained with Benedicks' electrolyte; also that contamination by sulphides seems to have had somewhat less effect on the FeO, and more effect on the MnO, determinations than was the case when Scott's electrolyte was used.

The results obtained by the three cooperators who used Fitterer's electrolyte vary considerably in some of the determinations of SiO_2 and Al_2O_3 and in most of the determinations of MnO. The statement was made (cooperator 3) that previous work (unpublished) with steels containing 0.60 to 0.80 percent of carbon indicated that the annealing

temperature had a tremendous effect on the value obtained for silica. Accordingly, samples of the eight steels were run in the "as-received" condition and after annealing for at least 12 hours at 650° C. The data in table 13 show that this treatment affected the silica results for only two steels, 2 and 6, with carbon contents in excess of 0.4 percent; that the results for alumina were not appreciably affected; that the results for MnO were improved, by bringing them into better agreement with those obtained by other cooperators with samples that had not been heat treated. The opinion was expressed (cooperator 3) that "the electrolytic method must be considerably modified if steels above about 0.35 percent carbon are investigated. There is also the possibility that the results on lower carbon steels might be affected by the heat treatment."

Styri's electrolyte was used for the determination of SiO_2 and Al_2O_3 (cooperator 12) and also to observe the effect on these determinations of structural changes produced by quenching the samples from 1,100° C in brine. The data indicate no marked effect on the results for silica and alumina. For the samples, as received, the determinations of silica yielded good results for five of the steels, high results for steels 2 and 6, and somewhat low results for steel 5. Reasonable values for alumina likewise were obtained, except for steel 4.

More data are needed to establish the accuracy of the electrolytic method. One of the items which should be studied further is the question of anodic oxidation. Cooperator 20 reported the formation of pentabromacetone at the anode during electrolysis and considered this a possible source of anodic oxidation of the sample. The good results obtained with improved methods of purification of the electrolytic residue prior to analysis (cooperators 4 and 35) serve to emphasize the need of further work of this kind.

6. MISCELLANEOUS METHODS

Three reports on the results of microscopic examination were submitted; a "cleanness rating" of the eight steels, based on an inclusion count according to Epstein's method (cooperator 1); and two extended microscopic studies (cooperators 23 and 26). However, these have not been of particular value in the quantitative determination of the oxygen content of these steels.

Few data are available on the oxide content of the eight steels, obtained by the mercuric-chloride, chlorine, fractional vacuum-fusion, nitric-acid, and hydrochloric-acid methods (table 14). In view of the limited number of data available for each of these methods, the most practical comparison is with the selected values for the iodine method, shown at the bottom of each section of table 14.

TABLE 14.—*Results obtained by the mercuric-chloride, chlorine, fractional vacuum-fusion, nitric-acid, and hydrochloric-acid methods*

Method	Cooperator	STEEL 1	2	3	4	5	6	7	8
DETERMINATIONS OF Al_2O_3 (%)									
Chlorine	15				0.002				0.024
	17	nil	0.004	0.001	.003	<0.001	0.001	0.001	.008
	20	0.006	.012	.003	.003	.003	.005	.023	.042
Fractional vacuum-fusion	24	.0075	.002	.0095	.0085	.002	.002	nil	.0095
Nitric acid	9	.001	<.001	<.001	.0015	<.001	.002	.003	.027
	13			nil	.0055			.002	.033
Hydrochloric acid	13							.002	
	29	<.001	<.001	<.001	.0035	.001	.001	.0015	.030
	35	.002	.004	.0035	.0066	.002	.003	.0025	.031
Best values from aqueous-iodine method		0.002 ±.002	0.002 ±.002	0.002 ±.002	0.006 ±.002	0.002 ±.002	0.002 ±.002	0.002 ±.002	0.030 ±.003
DETERMINATIONS OF SiO_2 (%)									
Chlorine	15	0.001	0.015	0.016	0.001	0.016	0.008	0.001	0.004
	17	.001	.096	.012	.003	.019	.007	.005	.009
	20	.003	.025	.020	.012	.019	.015	.004	.011
Fractional vacuum-fusion	24	.003	.011	.007	.002	.013	.004	.0055	.017
Nitric acid	9	.008	.0015	.011	.011	.014	.007	.011	.013
Hydrochloric acid	35	.001	.013	.0035	.004	.014	.0095	.002	.004
	29	.001	.001	.001	<.001	.012	.002	<.001	.001
Best values from aqueous-iodine method		0.003 ±.002	0.009 ±.003	0.005 ±.002	0.002 ±.002	0.016 ±.003	0.009 ±.003	0.002 ±.002	0.003 ±.002

DETERMINATIONS OF MnO (%)

DETERMINATIONS OF MnO (%)

Mercuric chloride	20	0.004	0.004	0.012	0.004	0.006	0.004	0.050	0.005
	25	.0015	.0025	.010	<.001	<.001	.0015	.012	<.001
Chlorine	17	.001	.025	.005	.007	.0075	.011	.0035	.011
Fractional vacuum-fusion	24	.058	.027	.049	nil	.018	.013	(*)	.009
Nitric acid	9	<.001	<.001	.003	<.001	.001	nil	<.001	.001
Best values from aqueous-iodine method	----	0.002 ±.002	0.004 ±.002	0.012 ±.004	0.002 ±.002	0.004 ±.002	0.008 ±.003	0.025 ±.005	0.003 ±.002

DETERMINATIONS OF FeO (%)

Mecuric chloride	20	0.290	0.038	0.284	0.061	0.068	0.043	0.630	0.288
	25	.313	.135	.323	.316	.115	.135	.720	.472
Chlorine	17	.001	.013	.005	.002	.007	.019	.068	.023
	20	.013	.035	.040	.040	.034	.037	.187	.024
Fractional vacuum-fusion	24	.009	.0045	.007	nil	nil	nil	*.449	nil
Nitric acid	9	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001
Best values from aqueous-iodine method	----	0.012 ±.004	0.013 ±.005	0.011 ±.004	0.004 ±.002	0.010 ±.004	0.010 ±.004	0.39 ±.03	0.014 ±.005

* In the analysis of iron 7, by the fractional vacuum-fusion method, FeO and MnO were determined together and reported as FeO.

(a) MERCURIC-CHLORIDE METHOD

In the mercuric-chloride method, the sample is subjected to the action of an aqueous solution of mercuric chloride, 120 g per liter, in the absence of air, until the reaction, $Fe+2\ HgCl_2=FeCl_2+2\ HgCl$, is complete. FeO and MnO remain in the insoluble residue. Compounds of manganese and iron with phosphorus, sulphur, and nitrogen are not decomposed quantitatively. The presence in the insoluble residue of these compounds, or of metallic particles from incomplete decomposition of the sample, leads to high results for FeO and MnO. The determination of SiO_2 and Al_2O_3 is not attempted.

The results for FeO of the two cooperators (20 and 25) using this method for the eight steels are consistently higher than those obtained by any other method. High contents of phosphorus and sulphur might account for the high values for FeO in steel 3, but the equally high values obtained for other steels, with lower phosphorus and sulphur contents, indicate contamination of the residue by particles of metal. Contamination of the residue by phosphides and sulphides would produce high values for MnO as well as FeO; on the other hand, contamination by particles of metallic iron would produce high values for FeO but would not appreciably affect the determinations of MnO. The two sets of values for MnO are in good agreement, except for iron 7 and, furthermore, are usually in agreement with the selected results by other methods. This indicates that the presence of metallic particles in the residue, from incomplete solution of the sample, is a more serious source of error than the presence of the phosphide and sulphide compounds in these eight steels.

(b) CHLORINE METHOD

In this method of analysis the sample is heated several hours at a moderate temperature in a stream of purified chlorine, whereby the metallic constituents are converted to chlorides, which are largely volatile under the conditions obtaining, whereas the oxide constituents are not attacked. These are then determined by suitable means in the residue from the chlorination treatment.

Determinations of SiO_2, Al_2O_3, and FeO were made on samples chlorinated at 350° C (cooperator 20) and at 500° C (cooperator 17). In addition, SiO_2 was determined on all the steels, and Al_2O_3 on two of them, chlorinated at approximately 380° C (cooperator 15). MnO was determined by one cooperator (17) on steels chlorinated at 500° C.

Approximately half of the results for SiO_2 are in good agreement with those by the iodine method, and those for Al_2O_3 also in reasonable agreement, although occasional high and low values were obtained. The values for FeO obtained on samples chlorinated at 350° C (cooperator 20) are consistently higher than those on samples chlorinated at 500° C (cooperator 17). The latter are consistently in good agreement with results by the iodine method. The high results for FeO after chlorination at 350° C suggest contamination of the residue in this case by particles of undecomposed sample. Both cooperators reported low values for the FeO content of iron 7. Determinations of MnO by the chlorine method (cooperator 17) are not in consistent agreement with the results obtained by other methods.

(c) FRACTIONAL VACUUM-FUSION METHOD

This modification of the vacuum-fusion method is based on the assumption that the oxides in a steel can be separated according to the temperatures necessary for their reduction. The FeO in a steel can be completely reduced at 1,050° C, whereas temperatures of 1,170, 1,320, and 1,570° C, respectively, are necessary for the reduction of MnO, SiO_2, and Al_2O_3. The sample, to which tin has been added to lower the melting point, is maintained at each of these temperatures successively, and the amount of gas evolved at each is used to indicate the amount of one of the oxide constituents.

Only one set of results (cooperator 24) is available. The results for SiO_2 and Al_2O_3 are generally in good agreement with the selected values by the iodine method. For steels 7 and 8 somewhat high results for SiO_2 are compensated by low results for Al_2O_3, indicating faulty separation of the two fractions in these two determinations. The values for FeO obtained in the fractional vacuum-fusion method are in good agreement with, or somewhat lower than, the iodine results. The high value for FeO in iron 7 represents the sum of the FeO and MnO, as the two constituents were not separated in this determination. The MnO values indicated by the fractional vacuum-fusion analyses are consistently higher, sometimes appreciably so, than the values obtained by other methods. These high values for MnO by the fractional vacuum-fusion method, particularly for steels 1, 2, and 3, perhaps explain the low recoveries of oxygen by the iodine method, as compared with the results by vacuum-fusion. However, determinations by one observer cannot be unreservedly accepted, according to the evidence of the data assembled in these cooperative analyses. Further information is needed to establish the accuracy of the fractional separations and the reproducibility of results by the fractional method in the hands of different operators. In the previous discussion of the vacuum-fusion method, the values for total oxygen obtained by the fractional method were compared with the selected values for the regular vacuum-fusion method. For five of the eight steels the fractional method yielded satisfactory values for total oxygen, but for the other three steels high results were obtained.

(d) NITRIC-ACID METHOD

This method depends upon the solubility of metallic constituents and the relative insolubility of oxides, particularly alumina, in approximately 10-percent nitric acid.

Values for Al_2O_3 that are in excellent agreement with selected results by other methods were obtained by two cooperators (9 and 13), but the determination of SiO_2 was less satisfactory, the results being too high, unless the hydrated silicic acid, formed during the solution of metallic silicides, was completely separated from the SiO_2 and silicate inclusions in the residue. On the other hand, low results for SiO_2 may be caused by partial solubility in the acid medium of some of the silicates that may occur in steel. Determinations of FeO and MnO by the nitric-acid method were made (cooperator 9) to illustrate the accepted belief that the method is not applicable to those determinations. The results demonstrate the almost complete solubility, in nitric acid, of FeO and MnO as they exist in these eight steels.

(e) HYDROCHLORIC-ACID METHOD

In this method diluted hydrochloric acid, approximately two volumes of water to one of concentrated acid, is employed to separate the metallic from the oxide constituents. SiO_2 and Al_2O_3 are determined in the insoluble residue, but the method is not applicable to the determination of FeO and MnO.

The values for alumina by this method are in excellent agreement with those by the iodine method, but the determinations of SiO_2, as in the nitric-acid method, may be affected by the partial solubility of certain silicates or by the presence of hydrated silicic acid. The determinations of cooperator 35 for both SiO_2 and Al_2O_3 are in excellent agreement with the selected values.

III. AUTHORS' COMMENTS AND CONCLUSIONS

The first impression derived from a study of the data of these cooperative analyses usually is that the results as a whole are decidedly unsatisfactory and indicate that none of the methods for determining oxygen or oxides is sufficiently accurate to conform to the requirements of modern metallurgical analysis. On the whole, however, the variation in results obtained in these cooperative determinations of oxides and oxygen is of about the same order of magnitude as is obtained in determinations of other elements, such as carbon, manganese, nickel, chromium, et cetera, when present in very small amounts.

The results of the vacuum-fusion method are in better agreement among themselves than are those obtained by the aqueous-iodine method. However, in consideration of the data obtained by the latter method, further allowance should be made for the complicated procedure and the number of operations that must be performed in one analysis. The approximate magnitude of the best results by the vacuum-fusion method is clearly indicated by the data for each steel. Some of the selected values for the aqueous-iodine method likewise are clearly indicated by concordant results, but in other determinations the lack of concordant data introduces an element of uncertainty in the selection of best values. The upper and lower limits of the acceptable ranges, to include permissible variations from the selected values, represent the considered opinion of the reviewing committee. It is recognized that there may be differences in opinion as to the proper location of some of the acceptable ranges. Raising or lowering the range as a whole, by one or two thousandths of 1 percent, in several cases would appreciably affect the number of cooperators who obtained acceptable results by the vacuum-fusion method.

The conclusions derived from detailed consideration of the cooperative data may be summarized, as follows:

1. The vacuum-fusion method yields accurate results for all eight of the steels, and the best results obtained by this method probably are close approximations of the true oxygen contents of each of the steels. Recommendations have been made in regard to the procedure and apparatus to be employed in order that the best results may be obtained. SiO_2 and Al_2O_3, as they occur in these steels, are completely reduced in the vacuum-fusion procedure; the error resulting from interference of manganese, at least up to 1 percent of manganese, is not

so serious with the recommended form of apparatus as it was formerly considered to be. The chief cause of erratic results appears to be spattering of the sample, during melting or shortly thereafter. A convenient and reliable means of eliminating this source of error is not yet available.

2. The aqueous-iodine method yields accurate results for aluminum-killed steels and for some silicon-killed steels but for others, especially steels of the rimming type, low results are obtained. The data for steels 1, 2, and 3, and to a lesser extent for iron 7, show clearly that the aqueous-iodine method cannot be relied upon for determining the total oxygen content of all steels. Part of the discrepancy may be due to some of the oxygen being present in the form of dissolved or entrained gases that are not recoverable by residue methods. Further efforts in standardization of the method, down to minute details of procedure, undoubtedly will result in improved agreement in the results obtained by different analysts. Further study of the determinations of FeO and MnO is particularly needed, and the need for greater accuracy in the chemical analysis of the small amounts of insoluble material obtained in the residue methods is to be emphasized.

3. None of the other methods is represented by sufficiently concordant data to justify the drawing of definite conclusions. The hydrogen-reduction method yields results of the same order of magnitude as the vacuum-fusion results, but further work to standardize the procedure of the hydrogen-reduction method is necessary. Likewise, the results of the other residue methods are of the same order of magnitude as the results obtained by the aqueous-iodine method and are more accurate for the determination of Al_2O_3 and SiO_2 than for FeO and MnO. Further standardization of the methods is desirable.

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A NEW PHENOMENON IN THE SUPERCONDUCTING TRANSITION OF TANTALUM AND OF TIN

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ABSTRACT

The transition from the superconducting to the normal resisting state under certain conditions is found not to be continuous but to include a hitherto unsuspected spontaneous increase in resistance followed by a slower decrease. The spontaneous decrease in resistance usually proceeds for several minutes in a succession of steps until only a fraction of its crest value remains. This crest value of the transient resistance is sometimes 75 percent of the normal. After such an effect has occurred, it will not occur again when the same conditions are reestablished, unless, in the meantime, the temperature has been lowered or else a time interval of at least half an hour has elapsed.

These spontaneous changes in resistance can be initiated by a step upward in temperature, in current, or in magnetic field and proceed thereafter, as described above, while all three external conditions are maintained constant. The combination of temperature, field, and current at which this phenomenon appears has been studied, and the progress of the resistance change under various conditions noted. The effect is pronounced only when the current is relatively large (about 2 amp in the tin wire, diameter 0.022 cm).

The transition temperatures of two specimens of hard-drawn tantalum wire were found to be 3.961 and 4.068° K, respectively. The presence of a transverse magnetic field depressed the transition temperature at a rate of 1° K per 1,250 oersteds.

CONTENTS

		Page
I.	Introduction	295
II.	Characteristics of specimens	296
III.	Nature of overshoots	299
IV.	Magnitude and speed of overshoots	300
V.	Persistence of resistance after an overshoot	302
VI.	Secondary overshoots	302
VII.	Interrupted overshoots	307
VIII.	Conditions for producing overshoots	307
IX.	Discussion	312

I. INTRODUCTION

In recent experiments at the National Bureau of Standards, in which currents of sufficiently large value have been caused to flow in wires of tantalum and of tin, while the temperature, external magnetic field, or current was gradually changed so that the material passed from the superconducting to the normal resisting state, it was found that there was a transient appearance of resistance which spontaneously disappeared. As conditions were further changed the resistance made a second and permanent reappearance. For lack of a better term we here refer to this sudden and temporary increase of resistance followed by a decrease as an "overshoot." It is the purpose of this paper to describe these overshoots in some detail, and to set forth the conditions under which they were found to occur.

When the tin specimen was caused to pass from the superconducting to the normal resisting state by increasing the current, the value of the current required to produce the transition was such as to produce at the surface of the wire a magnetic field which, of itself, in the absence of the current, would restore the resistance.[1] On the other hand, both of the tantalum specimens studied exhibited a further anomaly, in that the permanent restoration of resistance by a current in the specimen occurred at a value of current much smaller than would have been expected from the magnetic field normally required to restore resistance. A similar anomaly has been noted in several alloys [2 3] and has recently been reported in "fairly pure" tantalum by Mendelssohn and Moore.[4] The fact that the normal tin specimen shows the transient overshoot effect in similar fashion to the abnormal tantalum would seem to indicate that the overshoot phenomenon is a general property of all superconductors and is not a peculiarity of the particular tantalum specimens in which we first observed it.

In this work the temperatures were deduced from the vapor pressure of the liquid helium bath in which the specimens were immersed. The results have been reduced to the Leiden scale of absolute temperatures by using the vapor-pressure formula $\log_{10}p = -3.024/T + 2.208 \log_{10} T + 1.217$ given in Leiden Communication no. 202, where p is the vapor pressure in centimeters of mercury and T is the absolute temperature. The values have been carried out to the nearest 0.001° K, because differences may be significant to this precision even if the absolute value of temperature is not.

The term "resistance" is used merely to denote the quotient obtained by dividing the difference of potential at the terminals of the specimen by the (direct) current flowing in it, without intending to imply that Ohm's law is obeyed. The difference of potential was observed directly by the deflection of a sensitive galvanometer connected to potential leads attached to the specimen near its ends. Suitable shunt and series resistors were used as needed to reduce the sensitivity of the galvanometer. Except where noted specially, the current through the specimen was not interrupted or reversed during the course of any one experiment. When necessary, small corrections for spurious thermoelectromotive forces were applied on the basis of the deflections observed when the current circuit of the specimen was open just before and just after an experiment.

II. CHARACTERISTICS OF SPECIMENS

Table 1 gives a summary of the more important characteristics of the three specimens examined. The tin wire was formed from an ingot of NBS "standard sample" material (99.99% pure) by extruding it at about 170° C through a steel die. The tantalum specimens were purchased in the form of hard-drawn wires from the Fansteel Co., in 1933. A spectrochemical analysis [5] of wire from the same spool as specimen 95 Ta indicated only small amounts (probably not over a few tenths percent) of Sn and Si and traces of Fe, Ca, Cl, and Cb. In view of this, the abnormally low transition temperatures and high

[1] This relation was suggested many years ago by one of the authors and has been confirmed by workers at Leiden for several pure metals. See Tuyn, J. Franklin Inst. 201, 379 (1926).
[2] W. H. Keesom, Physica 2, 35 (1935). Leiden Comm. No. 234f.
[3] Rjabinin and Shubnikov. Physik Z. Sowjet-Union 7, 122 (1935).
[4] Nature 135, 826 (1935).
[5] This analysis was carried out by B. F. Scribner, to whom the authors are greatly indebted.

resistance ratio "r" of these specimens are more probably caused by internal strain rather than by impurities.

TABLE 1.—*Characteristics of specimens*

	Specimen		
	8 Sn	95 Ta	10 Ta
Diameter of wire, cm	0.022	0.0075	0.0127
Length (approx.), cm	225	210	70
Material of supporting tube	Paper	Glass	Paper
Resistance at room temperature, R_1, ohms	8.3	95.0	10.6
Resistance at 4.2° K, R_n, ohms	0.0081	25.0	2.83
$r=R_n/R_1$	0.00098	• 0.26	• 0.26
Transition temp ($R=R_n/2$, small I), °K	3.724	• 3.961	• 4.068
Transition range (0.1 R_n to 0.9 R_n), °K	0.023	0.050	0.055
Magnetic field per 1° K depression of the transition, oersteds [6]	116	1,250	1,020
Current per 1° K depression of the transition, observed, amp	6.86	0.95	1.89
Current per 1° K depression of the transition, calculated, amp	6.4	23.4	32.3

• Meissner, Z. Physik **61**, 191 (1930), finds $r=0.050$ and $T=4.38$ for his purest sample.

The effect of a transverse magnetic field in depressing the transition temperature was studied in some detail in 95 Ta with the results shown in figure 1, in which the resistance is plotted against magnetic

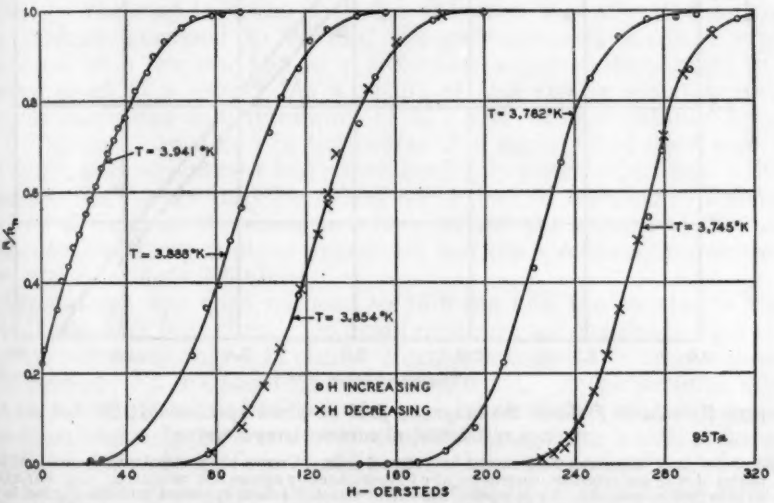

FIGURE 1.—*Variation with transverse magnetic field of the resistance.*

Variations are expressed as a fraction of the normal resistance above the transition range as measured with 1 ma (specimen 95 Ta) at various temperatures.

field for several different temperatures. These data show no measurable hysteresis. A single measurement on 10 Ta, incidental to other work, indicated that it had about the same dH/dT as 95 Ta. The tin sample showed hysteresis effects amounting to several oersteds.[6]

In figure 2 the solid circles show the external transverse field for half resistance at various temperatures, while the crosses show the

[6] In accordance with the formal action of the International Electrotechnical Commission in 1930 and of the International Union of Pure and Applied Physics, in 1932, we here use the name "oersted" for the cgs unit of magnetic-field intensity in place of the name "gauss", which is still frequently used for both this unit and that of magnetic-flux density.

values [7] of $2I_s/10\,a$, where a is the radius of the wire and I_s is the specimen current in amperes just sufficient to permanently restore half resistance. The precision in locating these points is considerably lessened by the transient effects to be mentioned below. Their systematic deviation from the line showing the effect of the external transverse field may perhaps result from an error in the measurement of the wire diameter. The agreement between the two sets of points is on the whole fairly close and strongly suggests that in this specimen

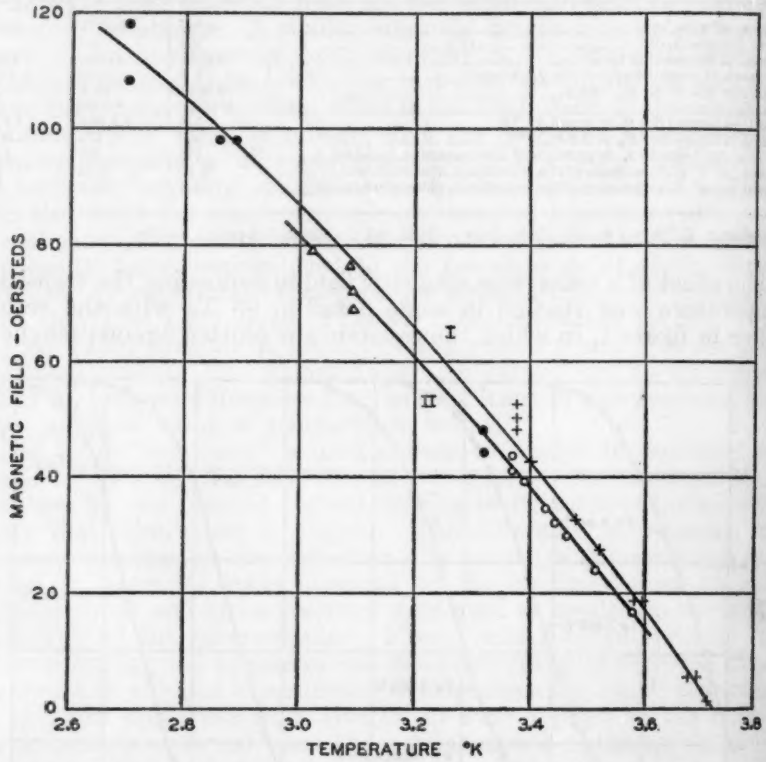

FIGURE 2.—*Curve I shows the magnetic field at which specimen 10* Sn *has one-half normal resistance, at various temperatures.*

Solid circles show transverse field caused by external coils. Crosses show circular field calculated from radius of wire and specimen current required to permanently restore half resistance. Curve *II* is locus of principal overshoots. Open circles show field calculated from specimen current required to initiate a principal overshoot. Open triangles show sum of external and specimen-current fields required to initiate principal overshoot.

the permanent restoration of resistance by the large currents is the result of the magnetic field which they produce.

In the tantalum specimens the effect of current in permanently disturbing the superconduction is shown in table 1 and also in figure 12, by the difference in trend of curves I and V. A small current is obviously far more effective in disturbing the superconduction than would be expected from its magnetic field.

The possibility that this abnormal sensitivity to current is a spurious result of a heating of the specimen above the temperature of the bath

[7] This quantity is of course the maximum intensity of the (circular) magnetic field produced at the surface of the wire by the current itself, if the current is distributed uniformly over the area or around the periphery of the wire.

was carefully studied but finally dismissed. The fact that the bare wire is in intimate contact with the liquid helium, the fact that the width of the transition range is substantially the same at large and small currents, and the fact that the depression in transition temperature varies in proportion to the current rather than to its square, all conspire to render this explanation very improbable.

III. NATURE OF OVERSHOOTS

The curious nature of the overshoots can best be made clear by following the course of a particular experiment. With specimen 95 Ta immersed in a bath of liquid helium held at a constant temperature of 3.877° K, and with no external magnetic field (other than terrestrial), the resistance when measured with a current of 1 ma was 0.0026 ohm. As the current was increased the potential difference increased at a still faster rate so that at 10 ma the resistance was 0.01 ohm; at 12 ma 0.024 ohm; and at 13 ma 0.059 ohm. After a few seconds, however, the resistance, with 13 ma still flowing, had decreased to 0.051 ohm, at which value it became steady. This small spontaneous change in resistance may be called a *preliminary overshoot*. As the current was further increased the resistance rose gradually so that at 16 ma it was 0.085 ohm and at 24 ma it was 0.20 ohm. However, when the rheostat in series with the specimen was adjusted so that the current increased to 25 ma, the galvanometer made a rapid excursion in a few seconds to a deflection which corresponded to a resistance of 17.0 ohms. As a result of this rise in resistance the current decreased to a minimum of 23.3 ma. The resistance began to fall again at once and in the course of a minute had decreased to 4.0 ohms, and the current had correspondingly risen to 24.7 ma. This spontaneous change may be called the *principal overshoot*. Further gradual changes in the rheostat setting raised the current to 25.5 ma without stimulating another overshoot, and the specimen then showed a resistance of only 3.5 ohms.

The current was then reduced to 15.6 ma and the resistance then found to be only 0.08 ohm. On again restoring the current to 25.5 ma, the resistance was only 0.11 ohm. Further increase in current showed 0.12 ohm at 27.5 ma and 0.16 ohm at 31.0 ma. A few seconds after this last reading was obtained, the resistance of the specimen again rose spontaneously to a crest value of 10 ohms, from which it immediately decreased, at first rapidly and then more slowly and with evident pauses at 7.1 ohms and at 6.2 ohms, to an apparently steady value of 2.9 ohms. Overshoots occurring subsequent to the principal overshoot, such as this later spontaneous change, may be called *secondary overshoots*.

The foregoing experiment involved an increase in specimen current at constant temperature and constant external magnetic field. Similar overshoots occur if the temperature is increased at constant current and field or if the externally applied field is increased at constant current and temperature, provided the specimen current is sufficiently high. Figure 3 gives a transition curve for specimen 95 Ta in which the temperature was varied. This curve does not happen to show any preliminary or secondary overshoots.

When the procedure was reversed and the specimen passed from the normal resisting to the superconducting state as a result of a decrease in temperature, field, or current, no abnormality was observed.

IV. MAGNITUDE AND SPEED OF OVERSHOOTS

If the final increment which stimulates the overshoot is very slight, the rate of rise of resistance is so slow that it can be followed even by the galvanometer used in this work, which had an (undamped) natural period of 4 seconds, but which was used with a shunt of such low resistance as to make it considerably overdamped.

If the variable is increased suddenly to a value considerably above the critical, both the increase and the initial stages of the decrease in resistance occur more rapidly, with the result that the maximum deflection of the galvanometer falls short of indicating the true maximum value of resistance attained. The rate at which the current, field, or temperature is changed prior to reaching the critical value,

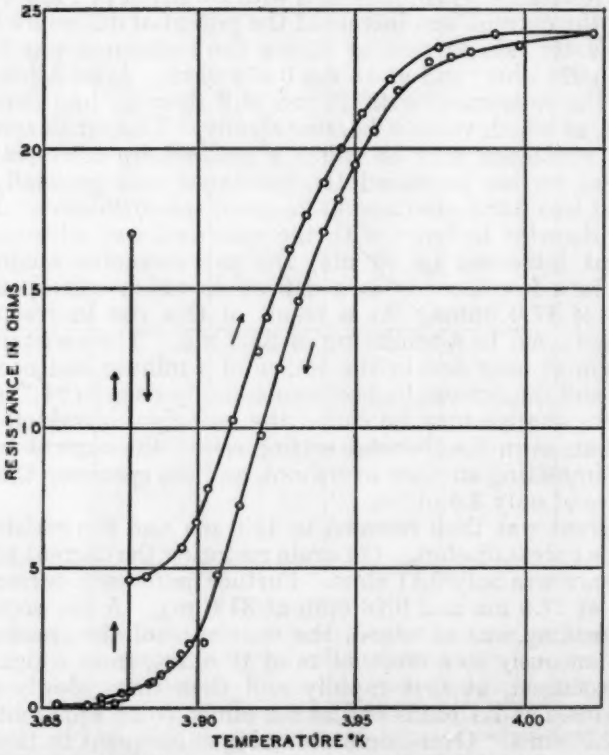

FIGURE 3.—*Typical principal overshoot and transition obtained by varying temperature of specimen 95* Ta.

does not seem to affect the overshoot. Figure 4 shows the resistance-time relation for a number of overshoots observed in specimen 95 Ta and figure 5 for an overshoot of the tin specimen 8 Sn. The maximum resistances observed in 95 Ta were sometimes approximately equal to the full normal resistance of the specimen but have never been found to exceed this resistance, even when the suddenly applied current was nearly four times the minimum value required to start an overshoot. They are more usually 25 to 50 percent of the normal resistance. In the case of specimen 10 Ta, the magnitude of the principal overshoots was notably less than in the case of 95 Ta, being usually about 14

percent of the normal resistance. In 8 Sn, the resistance at the crest of the overshoot was about 50 percent of the normal resistance.

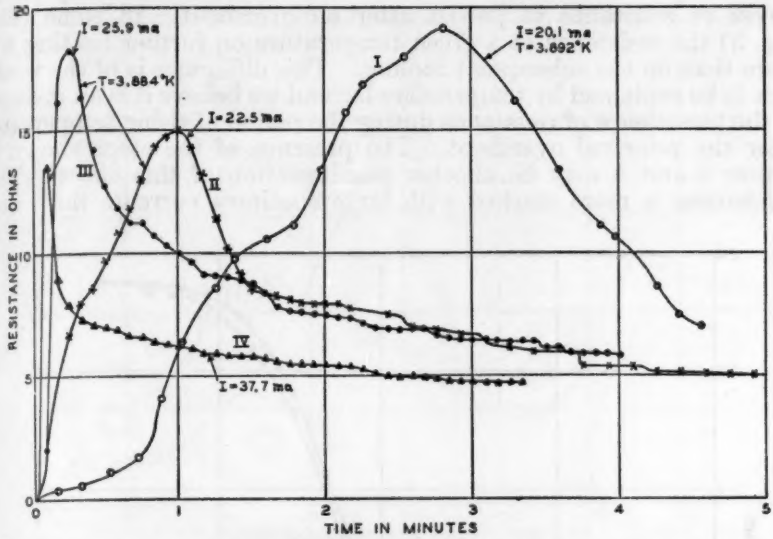

FIGURE 4.—*Typical overshoots in specimen 95* Ta, *after a current of the value marked on each curve has been suddenly applied.*

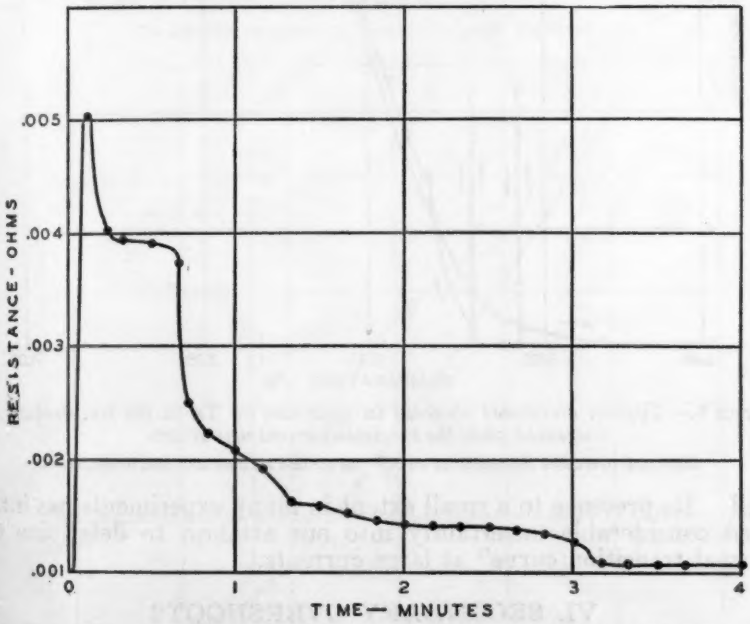

FIGURE 5.—*Typical overshoot in specimen 8* Sn *while held at 3.425°* K *when current was raised to 1.9* amp.

Figures 4 and 5 also show the definitely "stepped" character of both the increase (when it is slow enough to be observable) and the decrease in resistance.

V. PERSISTENCE OF RESISTANCE AFTER AN OVERSHOOT

In many of our experiments there seemed to be a tendency for an excess of resistance to persist after an overshoot. In some cases (fig. 3) the resistance at a given temperature on further heating was more than on the subsequent cooling. This difference is of the wrong sign to be explained by temperature lag and we believe it is an instance of the persistence of resistance during the period of rising temperature after the principal overshoot. The presence of the steps shown in figures 4 and 5 may be another manifestation of this effect. This persistence is more marked with large specimen currents than with

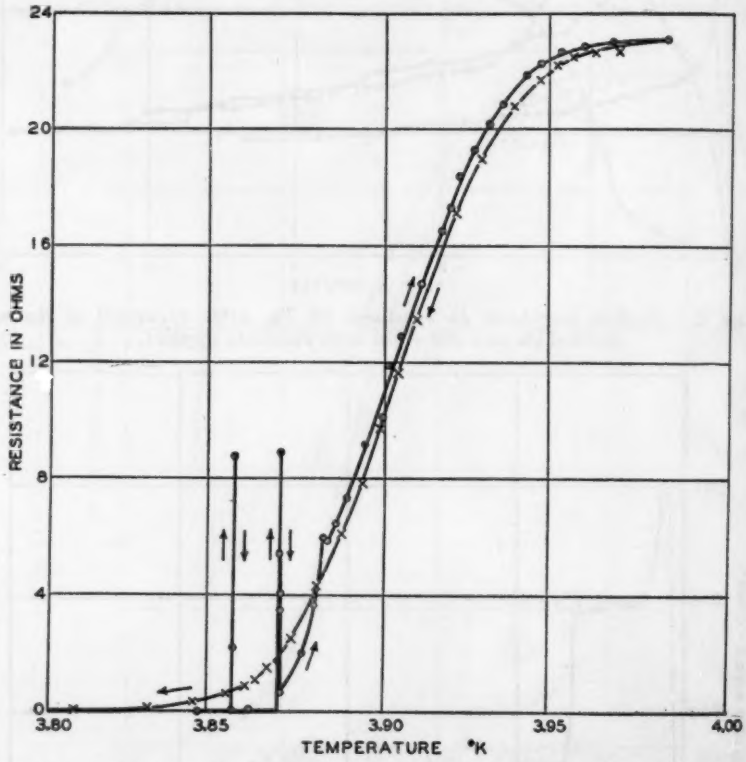

FIGURE 6.—*Typical overshoots observed in specimen 95* Ta *as the temperature was increased while the specimen current was 50* ma.

After each overshoot the specimen circuit was opened for 2 seconds and closed again.

small. Its presence to a small extent in many experiments has introduced considerable uncertainty into our attempt to determine the "normal transition curve" at large currents.

VI. SECONDARY OVERSHOOTS

After an overshoot has occurred and the resistance has settled down to a nearly constant value, the variable which stimulated the principal overshoot may be further increased. If this increase is made in abrupt steps, each sudden increase in the independent variable (that is,

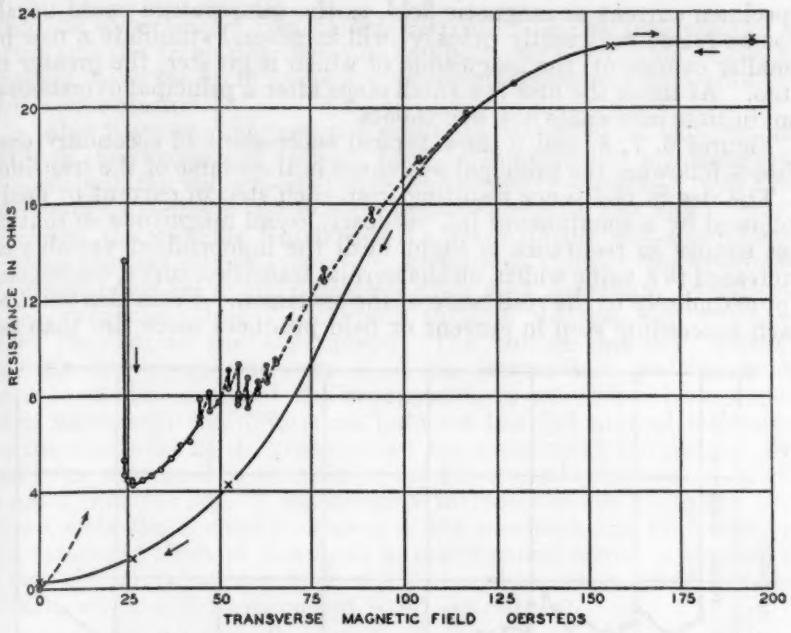

FIGURE 7.—*Typical principal and secondary overshoots observed in specimen 95* Ta *as the external transverse magnetic field was increased while the current in the specimen was 30* ma *and the temperature was 3.832°* K.

The specimen circuit was left closed throughout the experiment.

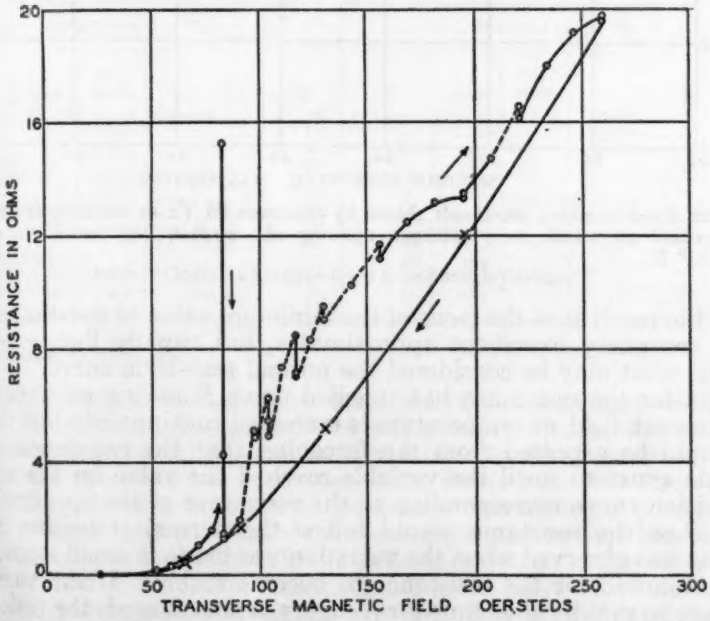

FIGURE 8.—*Typical principal and secondary overshoots observed in specimen 95* Ta *as the external transverse magnetic field was increased while the current in the specimen was 30* ma *and the temperature was 3.749°* K.

After each overshoot the specimen circuit was opened for 2 seconds and again closed.

specimen current or magnetic field, as the temperature could usually not be raised sufficiently quickly) will in general stimulate a new but smaller overshoot, the magnitude of which is greater, the greater the step. At times the first few small steps after a principal overshoot do not initiate noticeable new overshoots.

Figures 6, 7, 8, and 9 show typical successions of secondary overshoots following the principal overshoot in the course of the transition.

The rise in resistance resulting from each step in current or field is followed by a spontaneous fall[8] of nearly equal magnitude so that the net change in resistance is slight until the independent variable has increased to a value which, on the normal transition curve, corresponds approximately to the resistance of the specimen. From this point on, each succeeding step in current or field produces more rise than fall,

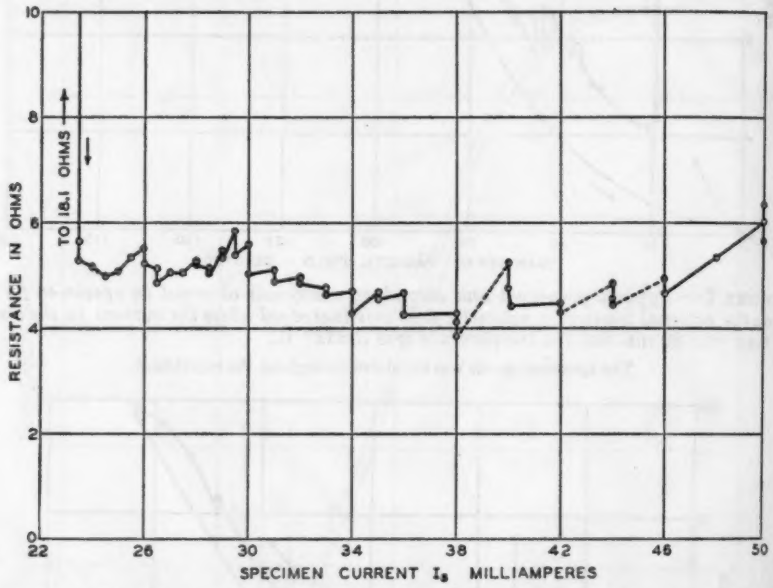

FIGURE 9.—*Secondary overshoots shown by specimen 95* Ta *as the current in it was increased in small steps without opening the circuit, the temperature being 3.894°* K.

The principal overshoot at 23.5 ma reached a crest of 18.1 ohms.

with the result that the locus of the minimum value of resistance after each secondary overshoot approximates, but usually lies somewhat above, what may be considered the normal transition curve.

If, after the resistance has steadied down following an overshoot, the current, field, or temperature is increased continuously but slowly, it would be expected from the foregoing that the resistance would remain constant until the variable reached the value on the normal transition curve corresponding to the resistance of the specimen and that then the resistance would follow the normal transition curve, just as was observed when the variation was made in small steps, time being allowed for the resistance to become stable. If the variation is made so rapidly that time for recovery is not allowed, the resistance

[8] This fall may in part be a further decrease in the resistance persisting from the principal overshoot. The sum of the falls during a succession of secondary overshoots, however, often exceeds the resistance persisting after the principal overshoot.

would be expected to rise as the current, field, or temperature is varied and the transition curve to lie above the normal curve but to approach it, as shown in figure 3. These expectations were borne out by the experiments.

In table 2 are summarized the results of a number of experiments in which the increase of current, field, or temperature has been carried nearly to the value needed to restore normal resistance. The first four columns indicate the experimental conditions, the entry "var" indicating the variable which was increased during the experiment. In those marked circuit "opened" the current through the specimen was interrupted for about 2 seconds after each secondary overshoot. In those marked "closed" the circuit through the specimen was kept closed throughout the experiment. The column headed "percent total increase" gives the sum of all the increases in the resistance observed in the course of the experiment, to which has been added (when necessary) the differences between the full normal resistance and the resistance at the point where the experiment terminated, the total being expressed as a percentage of the normal resistance. It will be noted that the sum of the separate increases seems to approach a value double the normal resistance of the specimen and that while it falls somewhat short of this limit in many experiments, it exceeds it by a significant amount only in the two experiments marked with an asterisk, which will be discussed later, footnote 10.

TABLE 2.–*Summation of increases in resistance during transition*

Temperature	Current	Field	Circuit	Total increase	Temperature	Current	Field	Circuit	Total increase
SPECIMEN 95 Ta					SPECIMEN 10 Ta				
°K	amp	Oersteds		%	°K	amp	Oersteds		%
var	0.030	0	Opened	208	3.994	var	0	Closed	152
3.758	.030	var	do	171	var	0.200	0	Opened	121
3.758	.060	var	do	190	3.962	var	0	do	144
3.862	var	0	do	*236					
3.880	var	0	do	*274	SPECIMEN 8 Sn				
var	.060	0	do	176					
3.718	.030	var	do	179					
3.840	.030	var	Closed	137	3.380	var	6.5	Opened	195
3.894	var[a]	0	do	185	3.524	var	0	do	167
3.894	var[b]	0	do	167	3.384	var	13	do	141
3.897	var	0	do	191	3.407	var	0	do	182
3.972	.030	var	do	201					

[a] Current raised in 4 large steps.
[b] Current raised in 20 small steps.

After a principal overshoot has once occurred, a moderate decrease of the current through the specimen will produce a very considerable decrease in the resistance, and in particular after the current circuit through the specimen has been opened for about 2 seconds and again closed, the resistance is found to be usually less than 0.5 percent of the full normal value and hence substantially equal to that before the overshoot occurred. Although the resistance is again the same the condition thus produced in the specimen must however be different from that immediately preceding the principal overshoot because now no overshoot results when the current, magnetic field, or temperature is restored to the value which stimulated the original overshoot. Sufficient further increases in current, magnetic field, or

temperature will however initiate secondary overshoots. In some cases, figure 6, the value of resistance just prior to one of these secondary overshoots has been found to be less than that estimated for the normal transition, as if the specimen was in an unstable state.

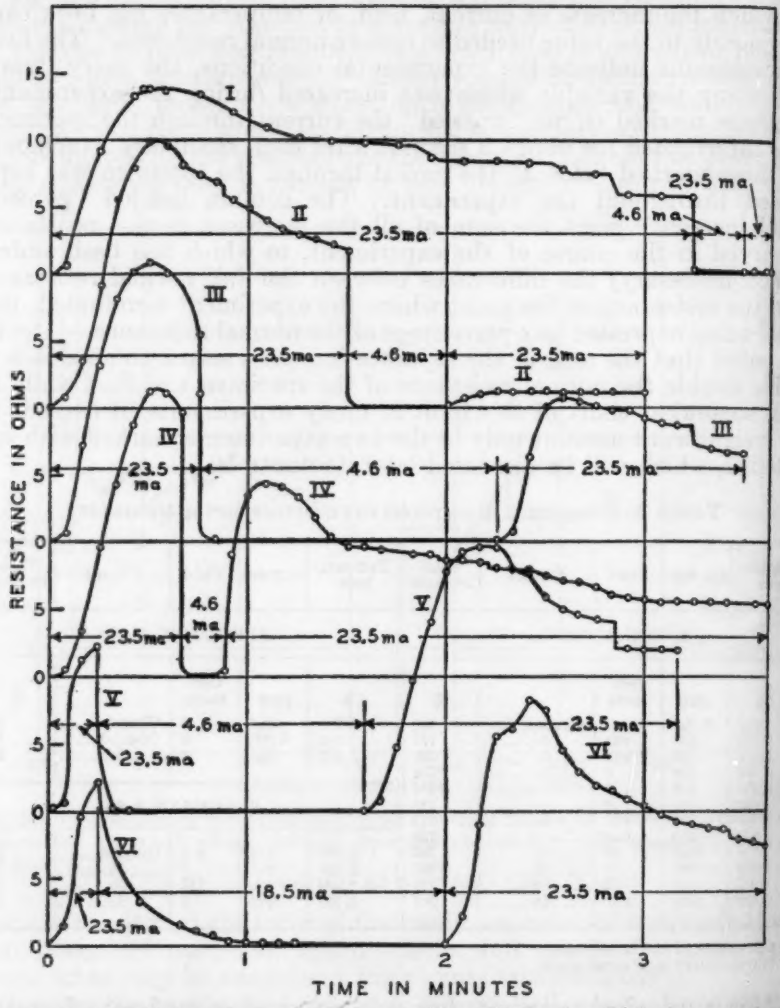

FIGURE 10.—*Interrupted overshoots in specimen 95* Ta *in which the current was reduced from the initiating value to a lower value during part of the phenomenon and then restored, as indicated by the horizontal dimension lines.*

Temperature=3.886° K.

Meissner [9] also has reported a case in which on raising the temperature the resistance remained abnormally low well into the transition range.

[9] Z. ges. Kälte-Ind. 41, 129 (1934). Physik Z. 37, 449 (1936).

VII. INTERRUPTED OVERSHOOTS

A number of experiments were performed with specimen 95 Ta in which a slow overshoot was initiated by applying a current only slightly above the critical, and the overshoot process was then interrupted by suddenly reducing the current to a lower value at some time before its completion. After an interval the original value of current was restored and the further change in resistance followed. Figure 10 shows the results. Similar results, not shown in the figure, were obtained in experiments in which the current in the specimen and the temperature were left unchanged, but in which the applied transverse magnetic field was removed quickly during the progress of an overshoot and then restored at a later time. It will be seen that the ability to produce an overshoot at the original current is not lost until the process has gone nearly to completion, and that the overshooting process requires the continued presence of the condition which initiated it, if it is to complete itself.

However, it was found that if the current was supplied by a battery through a circuit having little resistance other than that of the specimen itself, the process went to completion in spite of the automatic decrease in current as the resistance of the specimen rose and the increase in current as the resistance fell.

VIII. CONDITIONS FOR PRODUCING OVERSHOOTS

If the three independent variables, temperature, field, and current, are plotted along three mutually perpendicular axes, the locus of combinations of these variables at which a principal overshoot occurs will constitute a surface in three-dimensional space. This *principal critical surface* is fairly definite and reproducible and an overshoot will occur, with the exception noted below, if the state point representing the condition of the specimen is caused to move in any manner from the side corresponding to lower values of the variables to the other. The exception is that, as has been already pointed out, after a principal overshoot has taken place, if the state point is brought back through the critical surface by a reduction in current or magnetic field, which is then immediately increased again to its former value, a second overshoot does not occur. A second overshoot at the principal critical surface will occur only if the specimen has been restored to the normal superconducting condition. It was found that a convenient normalizing process was to lower the temperature by about 0.6° K. This, together with the time for raising the temperature again, lasted about 5 minutes. Fresh principal overshoots were obtained after reducing the temperature only 0.07° K below that at which the preceding principal overshoot had occurred. This occupied only 3 minutes. If the temperature was left at the value at which the overshoot occurred and the specimen current was reduced to zero, it was found that the ability to again produce a principal overshoot developed rather slowly. In the case of 95 Ta an interval of 10 minutes sufficed to make possible a second principal overshoot of one-third the previous magnitude, and 25 minutes one of one-half magnitude.

Figure 11 shows for specimen 95 Ta the contours of this principal critical surface for several constant values of T. Curve *IV* of figure 12 is a contour for $H=0$. Curves *I*, *II*, and *III*, figure 12, show for

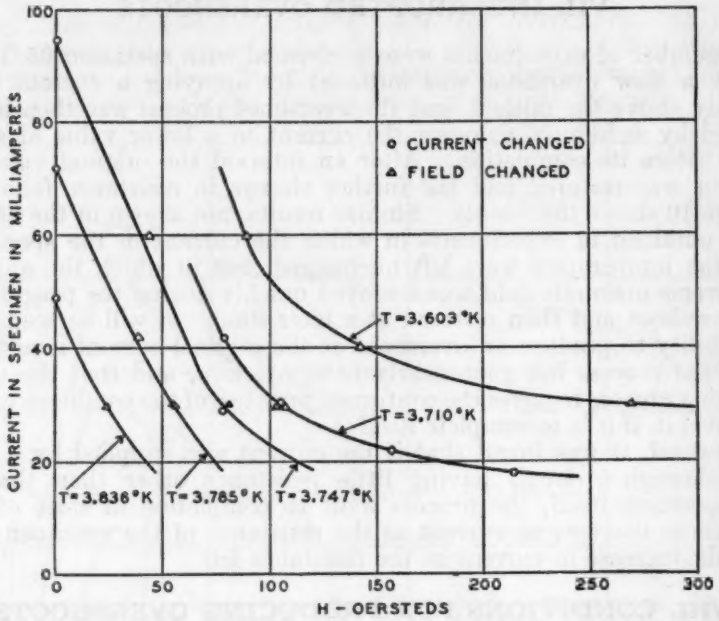

FIGURE 11.—*Contours of principal critical surface showing combinations of current and field at which overshoots occur for various fixed temperatures in specimen 95* Ta.

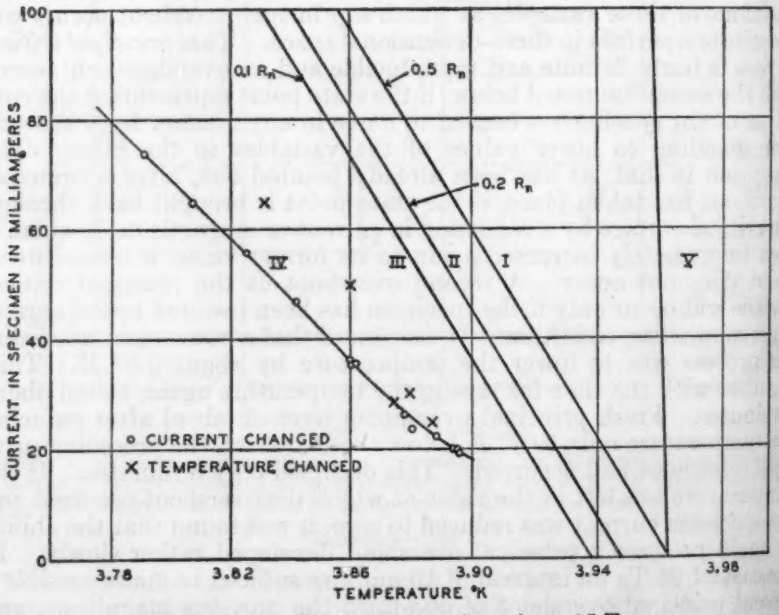

FIGURE 12.—*Characteristics of specimen 95* Ta.

Curves *I*, *II*, and *III* are the loci of combinations of current and temperature for zero external magnetic field at which specimen 95 Ta has 0.5, 0.2 and 0.1 of its normal resistance. Curve *IV* is the locus of combinations of current and temperature for zero magnetic field at which principal overshoots are initiated. Curve *V* shows the trend to be expected in Curve *I* on the basis of the Silsbee hypothesis using the observed magnetic depression of the transition.

comparison the temperature-current relation for which 0.5, 0.2, and 0.1 of the normal resistance appears.

At low currents the overshoot locus lies at a temperature about 0.05° K below the middle of the normal transition. At large currents there is a temperature depression which is definitely greater than that shown by the lines of constant resistance (*I*, *II*, *III*). The disturbing effects of the overshoots, however, prevent any very precise determination of these latter lines. The observed resistance just before a principal overshoot starts was usually less than 1 percent of the full normal resistance.

In specimen 95 Ta when a considerable magnetic field (100 oersteds) was present and the temperature was correspondingly low, the principal overshoot was smaller than at low fields, but the later secondary overshoots were larger and sometimes exceeded the principal overshoot.

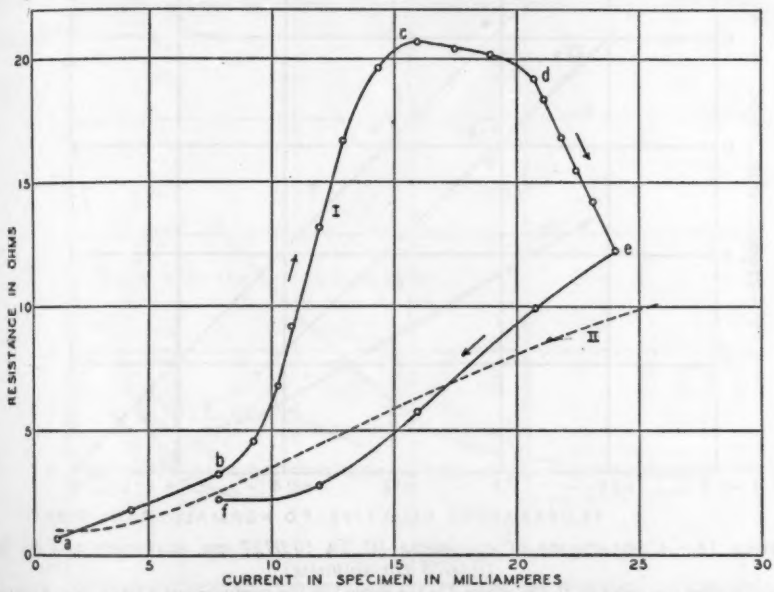

FIGURE 13.—*Curve I shows variation of resistance of specimen 95* Ta *with current at constant temperature of 3.926°* K.

From *a* to *b* the resistance values are stable in time. From *b* to *c* the resistance drifts upward spontaneously after each increase in current. From *c* to *d* the net drift is downward. Between *b* and *d* ordinates are the final values of resistance. Rheostat setting was left unchanged from *d* to *e*, while the resistance decreased spontaneously. Curve *II* shows the estimated position of normal transition curve.

In specimen 10 Ta with large magnetic field, the resistance came in continuously to a very considerable extent before the overshoot, which, in these cases, involved a change of only about 14 percent of the full normal resistance.

For currents of less than 18 ma and hence, if $H=0$, by curve *IV*, figure 12, at temperatures greater than 3.9° K, the overshoots in 95 Ta became less marked, though a tendency to slow drifts in resistance was observable down to 8 ma. Figure 13 shows the results of an experiment on 95 Ta at 3.926° K. The value of resistance appeared to be definite and free from spontaneous drifts up to currents of about 8 ma. For currents between 8 and 14 ma, each increase of current was followed by a drift upward in resistance which lasted for

several seconds and which seemed similar to the first stage of an overshoot but was not followed by a decrease in resistance. For currents greater than 14 ma, each increase in current was followed immediately by a drift downward in resistance, analogous to the later stage of an overshoot. At 20.8 ma the rheostat setting was left unchanged and a spontaneous decrease in resistance from 19.3 to 12.3 ohms, which occupied about 1 minute, caused the current to increase to 24.1 ma. On decreasing the current to 20.8 ma again, the resistance was only 10 ohms. The dotted line shows our best estimate of the normal transition curve in this range. With 1 ma only, the normal transition along a reproducible S-shaped, resistance-tempera-

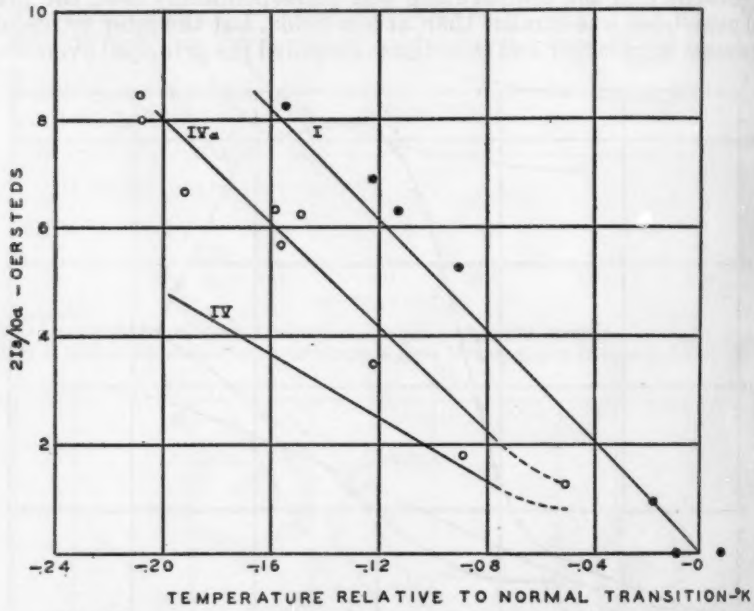

FIGURE 14.—*Comparisons of specimens 10* Ta (*0.0127* cm *diameter*) *and 95* Ta (*0.0075* cm *diameter*)

Ordinates show the value of $2I_s/10a$, where I is the current in the specimen and a its radius. Abscissas show the temperature in degrees Kelvin as measured from the normal transition temperature of each specimen. Solid circles indicate conditions under which specimen 10 Ta permanently attained half its normal resistance. Curve *I* shows corresponding values for specimen 95 Ta (reproduced from curve *I* of fig. 12). Open circles indicate conditions under which overshoots occurred in specimen 10 Ta. Curve *IV* shows corresponding values for specimen 95 Ta (reproduced from curve *IV* of fig. 12). Curve *IVa* is obtained from curve *IV* by multiplying each ordinate of the former by 1.7 (the ratio of the diameter of 10 Ta to the diameter of 95 Ta).

ture curve similar in shape to the resistance-field curves of figure 1, is observed.

In the tin specimen the *principal critical surface* approximates a plane, and has the further property that, at a given temperature, the values of specimen current I_s and external transverse field H_{ezt}, which in combination just produce the principal overshoot, obey the relation $2I_s/10a+H_{ezt}=$constant. It is, therefore, possible to represent the relations among the variables in two dimensions, by plotting as ordinate the total field $H=2I_s/10a+H_{ezt}$ against temperature. In figure 2 the values of total field at which the principal overshoot occurred are shown by open circles when the field was entirely caused by current in the specimen, and by open triangles when an external field and a considerable current were both present.

Measurements were made on specimen 10 Ta primarily for the purpose of finding the relation between the critical current for overshoots and the radius of the specimen by a comparison with data on 95 Ta. Unfortunately, the two tantalum wires seem to be somewhat different as is evidenced by the difference in their transition temperatures, which as measured in the absence of an applied field with very small currents, were 4.068 and 3.961° K, respectively. This difference may perhaps be the result of differences in internal strain in the two wires. A direct comparison of critical currents at the same temperature therefore appears meaningless and instead a comparison has been made at equal depressions below the transition

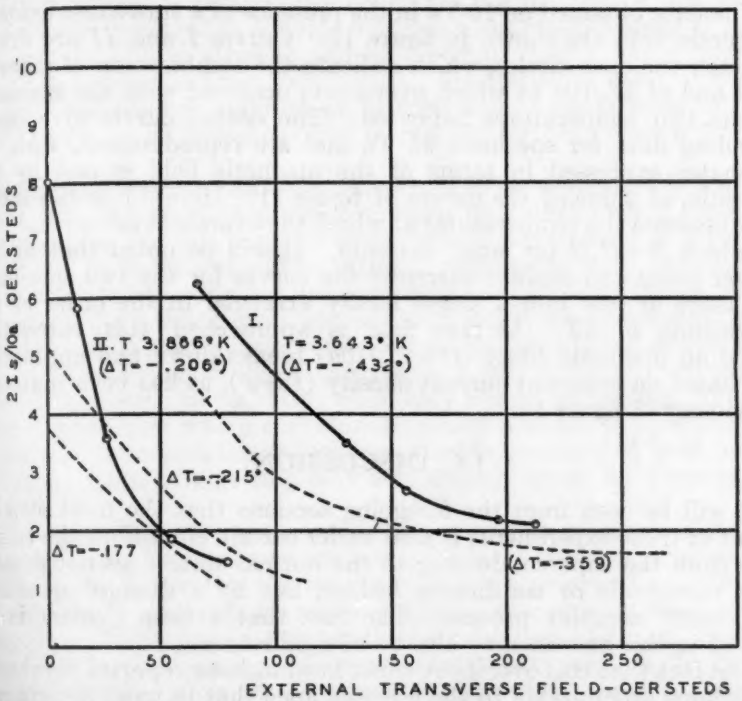

FIGURE 15.—*Curves I and II show the combinations of the circular magnetic field caused by the specimen current and the external transverse magnetic field at which overshoots occur in specimen 10* Ta (*0.0127* cm *diameter) at two fixed temperatures.*

The dotted curves show similar data for specimen 95 Ta (0.0075 cm diameter) reproduced from figure 11. The values of ΔT are the differences between the temperatures at which the overshoot occurred and the temperature at which $R=R_n/2$ for small currents.

temperatures, as observed with small currents. The comparison is shown in figures 14 and 15, in which the ordinates are the values of $2I_s/10a$. In figure 14, which gives the data in which no external magnetic field (other than terrestrial) was applied, the open circles show the values of $2I_s/10a$ at which 10 Ta showed its principal overshoot, while the solid circles show the values at which half its normal resistance had been permanently developed. Curve I is a reproduction of curve I of figure 12 but with its ordinates expressed in terms of magnetic field, to show the half-resistance curve for 95 Ta.

The agreement of curve *I* with the solid circles strongly suggests that the permanent attainment of resistance in the two wires of different diameter is connected with the magnetic field produced at the surface by the current. Curve *IV* is similarly a reproduction of curve *IV* of figure 12 showing the overshoot locus of 95 Ta, and obviously fails to agree with the open circles. However, if the ordinates of curve *IV* are multiplied by the ratio (1.7) of the diameter of 10 Ta to that of 95 Ta, curve *IVa* results. The agreement of *IVa* with the open circles indicates that in the two specimens of different diameter at a given temperature interval below their normal transition, the principal overshoot is stimulated when the apparent current density (that is, current in specimen divided by area of cross section) is the same.

The data obtained on 10 Ta in the presence of a transverse external magnetic field are shown in figure 15. Curves *I* and *II* are drawn through the open circles, which indicate the combination of external field and of $2I_s/10a$ at which overshoots occurred with the specimen at the two temperatures indicated. The dotted curves give corresponding data for specimen 95 Ta and are reproductions, with the ordinates expressed in terms of the magnetic field caused by the currents, of three of the curves of figure 11. Here ΔT is the difference between the temperatures at which the overshoot occurs and that at which $R=R_n/2$ for small currents. It will be noted that at the higher fields and smaller currents, the curves for the two specimens fall more or less into a single family arranged in the order of the magnitude of ΔT. As zero field is approached this correlation based on magnetic effect ($H=2I_s/10a$) breaks down and approaches one based on apparent current density ($I_s/\pi a^2$), as has been indicated previously in figure 14.

IX. DISCUSSION

It will be seen from the foregoing sections that the most striking result of these experiments is that under certain conditions the transition from the superconducting to the normal state does not proceed in a monotonic or continuous fashion but by a discontinuous and apparently complex process. The fact that a time element is involved in this process may also be of significance.

The fact that this overshoot effect has not been reported previously is perhaps attributable to the circumstance that in most experiments with superconducting wires, the current used to measure the resistance of the specimen has not been sufficiently large.

We may consider (as is very probable) that various parts of these polycrystalline specimens are not exactly equally favorably situated for exhibiting superconduction, and hence reach their thresholds for overshoots, as well as for the normal transition, at slightly different temperatures, fields, or currents. The overshoot phenomena may then be conveniently described in a self-consistent fashion by considering that in going from the superconducting to the normal resisting state, under the conditions which produce overshoots, the material passes successively through three distinct stages.

As temperature, field, or current is raised before the principal overshoot is reached, the bulk of the material is in the superconducting state, stage *A*. The specimen, as a whole, then has a small but measurable resistance. At the beginning of the principal overshoot,

conditions became such that for part at least of the specimen stage *A* is no longer stable, and this part passes to stage *B*. This stage which each part of the specimen passes through at the crest of its overshoot, is characterized by a relatively high resistance and a tendency to pass over spontaneously into a new state also of zero resistance, stage *C*. Stage *C* differs from stage *A* in the important respect that in it the overshoot phenomenon can not be initiated. The progress from *B* to *C* takes place more slowly than that from *A* to *B*.

The subsequent overshoots then correspond to the transitions of other portions of the specimen which remained in stage *A* during the preceding overshoots. On this basis, there is no fundamental difference in the mechanism of the principal and the other overshoots.

If the current is interrupted before all the material which would otherwise be involved in a single overshoot has reached stage *B*, some of it will be still in stage *A* and be ready to start a new overshoot when the current is again established. On the other hand, if all the material has reached stage *B*, an interruption of the current will not be followed by an overshoot but merely by further progress from *B* to *C*.

Since the specimen has been considered to be somewhat inhomogeneous, the production of a large overshoot by a small step in temperature, field, or current, suggests strongly that the passage of a part of the specimen from stage *A* to stage *B* propagates itself to adjacent parts which were nearly but not quite past their stability limits. This view that the phenomenon propagates itself is also consistent with the observation that a fast overshoot results from a large step beyond the critical frequency which can throw a larger number of centers beyond their limit of stability, while only a slow response is obtained from a small step which can stimulate only a much smaller number of centers from which the disturbance must be propagated over greater distances. Also a large step may well directly speed the propagation rate (fig. 4).

The view that different parts of the specimen reach their thresholds at slightly different temperatures, fields, or currents, implies that the resistance shown by the specimen before a principal overshoot is caused by the existence of sections which have already reached the normal resisting state, in series with other sections still superconducting. This preliminary resistance was particularly large in the case of specimen 10 Ta when in a magnetic field. Only those sections of the wire which are still in the superconducting stage *A* are supposed to be capable of exhibiting the overshoot phenomenon. In these sections it is to be presumed that by reason of the Meissner effect, the current is distributed in a thin layer around the outer surface of the wire.

If each portion of the specimen as it reaches stage *B* has temporarily its normal resistance, it would be expected that the sum of all the increases of resistance in these experiments would amount to double [10]

[10] The 4th and 5th experiments on specimen 95 Ta listed in table 2 seem to be exceptions to this. In the 4th experiment, the decrease in resistance following a third overshoot at 80 ma was abnormally great suggesting that the (manual) control of the bath temperature may have been unable to adjust for the sudden fluctuations in heat supply and allowed a temporary drop in temperature permitting some of the material to return to stage *A*. In the 5th experiment the increases in current were small with the result that the principal overshoot was very slow and that 13 successive secondary overshoots were recorded. The circuit was opened for 2 seconds after each overshoot to permit stage *C* to be more fully attained, and it may be that the long duration of the experiment permitted some of the material to pass back to stage *A* and go through the process again.

the normal resistance of the specimen, since the changes from A to B, as well as those from C, to the normal resisting state will be included. If, however, the external conditions are advanced rapidly, there is not time for the change from B to C to proceed to completion, and the sum of the increases in such an experiment is less than double the normal resistance.

After the completion of an overshoot the specimen has, in general, about as low a resistance as before it occurred, so that we may again expect that it contains sections of normally resisting material in series with sections of zero resistance, the former being the same as those existing previous to the overshoot and hence having been unaffected by it. The zero-resistance sections, however, are obviously different from the corresponding sections in stage A since they have lost the ability to overshoot at the originally critical conditions. It would seem possible that the distinction may be in a fundamental difference in the distribution of current over the cross section of the wire in the two stages. In stage A this distribution must (on the basis of the Meissner effect) be confined to the surface of the wire. In contrast to this the zero-resistance sections of the specimens in stage C may be thought of as a combination, in parallel, of normal resisting material and of superconducting filaments or laminas, as has been suggested by Gorter and other theoretical workers in a different connection. Such a more nearly uniform distribution of current over the cross section of the wire might well bring into service particularly favorably situated portions which had been inactive in the regime of stage A. It must be recognized, however, that this regime suggested as a possibility for stage C could not persist unless there is a sufficient range of threshold conditions to permit some of the outer portions to remain superconducting in spite of the somewhat increased magnetic field resulting from the new current distribution.

The propagation through the specimen of an initial disturbance may be reasonably explained as follows: when one volume element unfavorably situated for superconduction and located at the surface is subjected to a magnetic field and temperature which exceed its threshold it becomes resisting. The flow lines of current in avoiding this spot will necessarily be somewhat bent, with a corresponding local increase in magnetic field in adjacent volume elements; these, unless they possess abnormally high thresholds will in turn become resisting and increase the initial disturbance, as is required for propagation. With small currents the additional local field resulting from a given distortion of the flow lines will be small and the propagation of the disturbance will be readily checked by a chance group of favorably situated volume elements. This is in accord with the observation that a considerable current is requisite for the production of overshoots.

The recent experiments of de Haas and Guinau[11] on the penetration of magnetic field into a superconducting tin sphere show very definitely a complete breaking-down of one regime of macroscopic currents into a distinctly different system. It would seem that this process may be rather closely analogous to the overshoot phenomenon.

WASHINGTON, January 8, 1937.

[11] Physica 3, 182 and 534 (1936).

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OPTICAL ROTATION AND ATOMIC DIMENSION FOR THE FOUR OPTICALLY ACTIVE 1-HALOGENO-2-METHYLBUTANES [1]

By Dirk H. Brauns

ABSTRACT

The pure optically active 1-fluoro-, chloro-, bromo-, and iodo-derivatives of 2-methylbutane have been prepared and values of their optical rotation, specific gravity, refractive index, and boiling point at various pressures, determined. A classification of their active forms is made, and on this basis the numerical relation of the differences of molecular rotations of these compounds (Cl-F), (Br-Cl), and (I-Br) is 41:18.1:21.6, which is in substantial agreement with the numerical relation for the differences of the respective atomic radii of the neutral halogen atoms (41:16:21).

CONTENTS

	Page
I. Introduction	315
II. Experimental part	316
1. Preparation of pure compounds	316
(a) *l*-Rotatory-2-methylbutanol-1	316
(b) *l*-Rotatory-1-fluoro-2-methylbutane	320
(c) *d*-Rotatory-1-chloro-2-methylbutane	323
(d) *d*-Rotatory-1-bromo-2-methylbutane	324
(e) *d*-Rotatory-1-iodo-2-methylbutane	325
2. Properties of pure compounds	326
(a) Optical rotation	326
(b) Specific gravity	326
(c) Refractive index	328
(d) Boiling points at various pressures	328
III. Discussion of results	329
IV. Conclusions	331

I. INTRODUCTION

It has been established in the writer's previous investigations on this subject [2] that certain halogen derivatives may be divided into two classes. Those compounds which compose the first class have the halogen directly attached to an asymmetric carbon atom and differ only in having one halogen replaced by another. For these substances the differences of their *specific rotations* (Cl–F), (Br–Cl), and (I–Br) have the numerical relation 41:17:21, which agrees with the numerical relation 41:16:21, for the differences in atomic radii of the respective neutral halogen atoms. Those in the other class have the halogen atom attached indirectly (by a chain of atoms) to the asymmetric

[1] This article is the tenth contribution to a series on optical rotation and atomic dimension. The ninth article was published in BS J. Research 7, 573 (1931) RP358.

[2] Fifth article, J. Am. Chem. Soc. 47, 1285 (1925); ninth article, BS J. Research 7, 573 (1931) RP358.

carbon atom. For these latter substances the differences of their *molecular rotations* have a numerical relation which likewise agrees with that for the differences in atomic radii of the respective non-ionized halogen atoms. All the investigated compounds were carbohydrate derivatives which contain several asymmetric carbon atoms, so it was found desirable to prepare the halogen derivatives of two active amyl alcohols, 2-methylbutanol-1 and methylpropylcarbinol, for testing the above regularities, as these compounds are simple in structure and contain only one asymmetric carbon atom. The present paper reports the results obtained with the halogen derivatives of 2-methylbutanol-1, where the halogens are indirectly attached to the asymmetric carbon.

II. EXPERIMENTAL PART

1. PREPARATION OF PURE COMPOUNDS

(a) *l*-ROTATORY-2-METHYLBUTANOL-1

Since the beginning of the investigation of van't Hoff and Le Bel's postulate, as well as of Guye's hypothesis, derivatives of this alcohol have served for testing these theories. In the early days the active alcohol was prepared from fusel oil. This old, historical method has not been replaced by a better one, as the modern synthetic way for preparing active 2-methylbutanol-1 by the resolution of the racemic compound, obtained by the Grignard method, gives poor results.[3]

For separating the active amyl alcohol from the isoamyl alcohol, 3-methylbutanol-1, with which it is mixed in the fusel oil, Le Bel devised a method which has been applied by most investigators, although the final products were not more than about 85 percent pure, as was proved later by Marckwald and McKenzie,[4] who first obtained the alcohol in pure condition. Le Bel[5] found that the isoamyl alcohol was more easily converted to the chloride than 2-methylbutanol-1, and applied this observation for purification in the following manner: The fusel oil was saturated with hydrochloric acid and boiled under reflux or heated in sealed tubes for partially converting the mixture of the alcohols to chlorides, and finally fractionated for obtaining the unattacked alcohol. By repeating this process a fairly pure active amyl alcohol could be obtained, although the yield diminished appreciably by each treatment. Marckwald and coworkers[6] prepared the pure active 2-methylbutanol-1, and made several derivatives of it. Marckwald and McKenzie prepared the alcohol from beet-molasses fusel oil, which contains more active amyl alcohol (48 to 50 percent) than that from other usual sources (13 to 22 percent). The concentration was brought to 80 percent by the Le Bel method, and the pure, active 2-methylbutanol-1 obtained by recrystallization of the 3-nitrophtalic ester to constant melting point, followed by saponification and distillation. From the active amyl alcohol present in the fusel oil before treatment with Le Bel's process, Marckwald separated 5 percent in this way as pure alcohol. Klages and Sautter,[7] who repeated Marckwald and

[3] von Falkenhausen, Biochem. Z. **242**, 472 (1931).
[4] Ber. deut. chem. Ges. **34**, 485 (1901).
[5] Bul. assn. chim. [2] **21**, 542 (1874); [2] **25**, 545 (1876).
[6] Ber. deut. chem. Ges. **34**, 479, 487 (1901); **35**, 1595, 1602 (1902); **37**, 1038 (1904); **42**, 1583 (1909).
[7] Ber. deut. chem. Ges. **37**, 649 (1904).

McKenzie's method and checked their data, obtained only 2 percent of the original active alcohol in the pure form. The Pasteur process [8] for making active 2-methylbutanol-1, which is based on the recrystallization of the barium amylsulfate, was also studied by Marckwald, but the yield is not better and Marckwald recommended the first-mentioned method.

For the present investigation it was found desirable to have a larger amount (at least 1 liter) of pure active 2-methylbutanol-1 available for studying different methods for obtaining the pure optically active chloro-, bromo-, and iodo-derivatives, and further for preparing, if possible, the active fluoro-derivative. A large amount of pure optically active 2-methylbutanol-1 was obtained in the following way: One-hundred liters of fusel oil was prepared by the Rossville Co., Lawrenceburg, Ind., from cane sugar molasses which contained the largest possible amount of beet sugar molasses (beet sugar molasses alone cannot be fully fermented). This fusel oil was distilled from a steam-heated, tin-lined, copper fractionating still and gave 70 liters of amyl alcohol, a sample of which, in a 2-dm tube, gave the rotation, $\alpha = -4.0$ circular degrees (the pure optically active 2-methylbutanol-1 gives, in a 2-dm tube, $\alpha = -9.6$ circular degrees). This alcohol was put through the Le Bel process as described above, using borosilicate glass tubes in the beginning, and later, as some of the tubes cracked, a steel, glass-lined autoclave. Twenty-four liters of amyl alcohol having $\alpha = -5.4$ circular degrees (2 dm) was obtained. A second treatment gave 8 liters having $\alpha = -6.3$ circular degrees (2 dm). A third milder treatment gave 1.75 liters of amyl alcohol having $\alpha = -8.8$; 1 liter having $\alpha = -8.3$; and 2 liters having $\alpha = -7.3$, all in circular degrees, for a 2-dm tube. The satisfactory increase by the last treatment is due more to a careful fractionation than to chemical purification, thus indicating that the pure alcohol may be obtained by fractionation only. If this active amyl alcohol had to be prepared again, fractionation only would be applied. Industrial as well as laboratory fractional distillation has been materially improved in recent years, and this method of fractionation now gives far better results than were possible at the time of Le Bel, or even of Marckwald. High efficiency of separation is needed because the boiling point of isoamyl alcohol (131°) is not far from that of 2-methylbutanol-1 (128.9°).

The fractionating column (see fig. 1*a*), made of borosilicate glass, has an inside diameter of 15 mm, a length of 1.5 m, and, for thermal insulation, it is surrounded by a sealed-in high-vacuum jacket, integral with it, which is wound with asbestos cord. The column has three sharp dents at the bottom, supporting the filling of soft glass tubing (5 mm outside diameter, 1 mm wall thickness, and 6 to 8 mm long). The column is sealed at the lower end to a round flask of 500 ml capacity provided with a side tube for filling, in which is ground a tube drawn out at one end to a capillary and at the other sealed to a stopcock which is connected with a drying apparatus for supplying dry air to prevent bumping of the boiling liquid. The distilling flask, which is also insulated with asbestos cord, may be cleaned by heating with some distillate, which can be siphoned off through the side tube. The upper part of the fractionating column consists of a tube 15 mm in diameter with ground stopper from which a short thermometer is suspended. The lower part (160 mm) of this upper section is jacketed

[8] Compt. rend. 41, 296 (1873).

and may be cooled by blowing air through the jacket. However, this was not found necessary, as more conservation of heat was required, which was obtained by proper insulation. The lower half of this upper

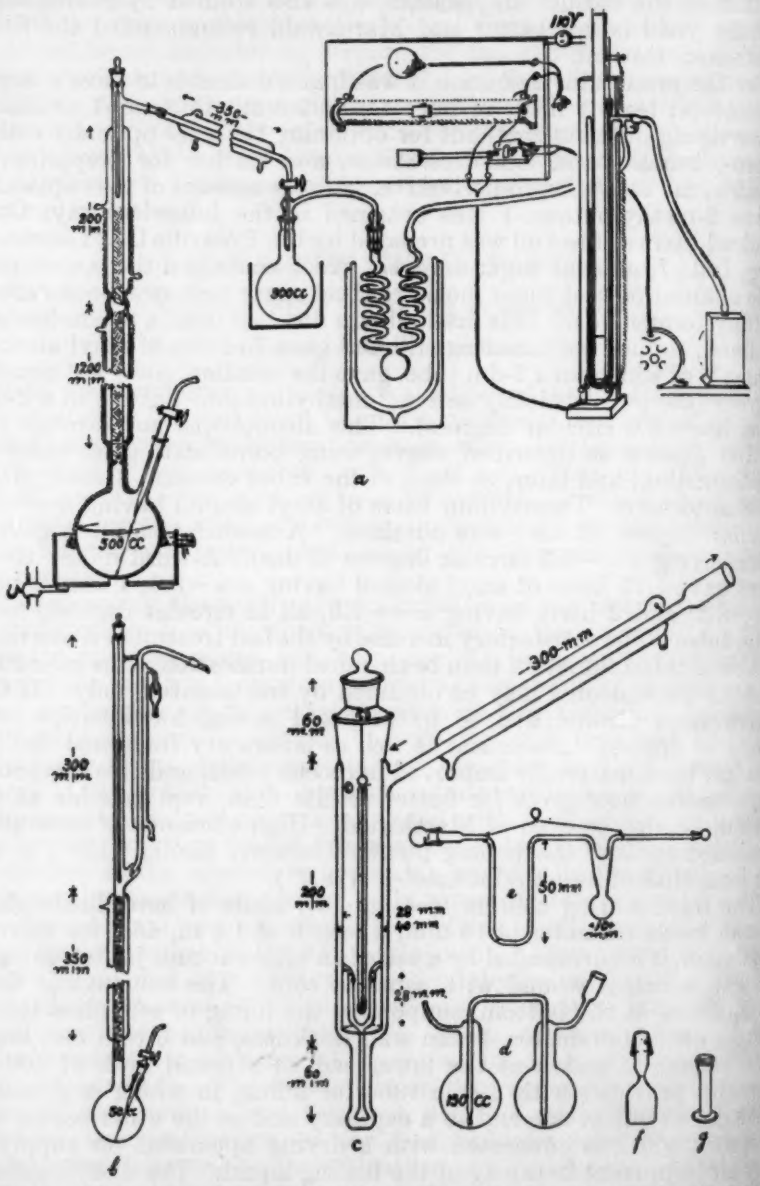

FIGURE 1.—(a) *Fractionating apparatus for methylbutanol-1;* (b) *fractionating apparatus for the halogen derivatives;* (c) *boiling-point apparatus;* (d) *double flask;* (e) *volatilizing apparatus for combustion;* (f) *picnometer;* (g) *steel tube for Parr bomb.*

section, which is slightly constricted at the bottom, is filled with pieces of soft glass tubing. This constricted part is connected by an inner seal into the upper part of the fractionating column, thus allowing the

observation of the rate of reflux. Above the jacket is a side tube provided with a ground joint for connection with the condenser, which in turn is connected by ground joints to the receiver and the spiral tube. The spiral tube cooled by ice water prevents the loss of distillate by evaporation in the vacuum. The manipulation of a stopcock permits changing of receivers without materially disturbing the vacuum in the column. All joints are accurately ground, no lubricant being used. The distillation pressure was maintained with a fluctuation of not more than 0.5 mm by a device described by H. L. Cox.[9] Some improvements were introduced as follows (see fig. 1): The glass tubes of the manostat were situated closer together so that a sliding rule between the tubes can be accurately read for obtaining the pressure; and further, the electric current passing through the manostat-manometer was obtained by reducing the 110-volt current to the proper value by an arrangement shown in figure 1 (*a*). A Hyvac oil vacuum pump was used.

The flask was heated by an electric heater constructed in the following way: A hemisphere of asbestos paper, made by using the next larger size round flask as a mold around which the wet mass of paper was built up and gradually loosened by a thin pliable spatula, was placed in a rectangular box of transite board, containing a circle of no. 20 nichrome wire, of triangular spiral cross section. This spiral was placed around the hemisphere of asbestos paper inside the box somewhat below the largest diameter by fastening to two binding posts near each other outside the box. The flask used for the molding was now clamped in place inside the asbestos hemisphere and the space between the transite walls and the asbestos paper filled with the proper mixture of water and plaster of paris and allowed to dry. The diameter of the inside hemisphere is about 11 cm, the width of the transite box 17 cm, and the height 9 cm. A hole 5 cm in diameter was then made in the center of the bottom of the box and also the plaster of paris beneath that hole carefully removed, leaving the asbestos lining intact. The heater was then wired on a ring clamp of suitable size by which it could be easily kept in place for heating the fractionating flask. The advantage of this heater is that bumping is minimized, as the heat energy is delivered nearer to the surface than to the bottom of the flask, which is kept comparatively cool. A substantially constant input of electrical energy, obtained from a storage battery, was used in order to secure a slow fractionation at constant rate (about 10 drops per minute). For collecting the so-called "hold-up" of the column at the end of a fractionation, which is especially desirable when small amounts are fractionated, as in the last fractions of the halogen derivatives, it is only necessary to apply suddenly a higher vacuum and remove the heater after the quick delivery of the distillate has stopped.

Two of the fractionating stills were constructed and could be operated simultaneously at the same pressure, using the one pressure-regulating system. The efficiency of these distillation columns, operating at a pressure of 150 mm of Hg, is indicated by the following figures, which give the optical rotation in a 2-dm tube, of middle fractions, corresponding to 50 percent of the charge, obtained from successive distillations: (1) −6.9° to −8.3°; (2) −8.3° to −8.8°; (3) −8.8° to −9.2°; (4) −9.2° to −9.3°; (5) −9.3° to −9.4°; (6) −9.4° to −9.5°;

[9] Ind. Eng. Chem., Anal. Ed. 1, 7 (1929).

and (7) −9.5°. After many series of such fractions there was obtained 1.35 kg of 2-methyl-butanol-1 having an optical rotation of −9.5° in a 2-dm tube.

The purity of our preparation of 1,350 g, based on Marckwald and McKenzie's value (see table 1) is about 98 percent. As the impurity is an optically inactive substance, our preparation seemed a sufficiently pure starting product for preparing the pure active halogen derivatives. This conclusion was further substantiated by the close agreement of the values obtained by Marckwald (and also by Klages and Sautter) for their active iodine derivative with the value obtained for the iodine derivative in this investigation.

(b) *l*-ROTATORY-1-FLUORO-2-METHYLBUTANE

The method of Moissan [10] and of Moissan and Meslans [11] for preparing the fluoro derivatives of the aliphatic alcohols by the action of silver fluoride on the iodine derivatives of the alcohols is used at the present time, with minor modifications. By his method Moissan prepared methyl, ethyl, propyl, and isobutyl fluorides. Paternò and Spallino [12] found that sec-hexyl fluoride and normal octyl fluoride can be prepared by the action of silver fluosilicate on the respective iodine derivatives, and they observed that the fluoro derivative of the secondary alcohol is liable to split off hydrofluoric acid, forming hexylene. Swarts [13] prepared the fluorides of primary and secondary heptyl and octyl alcohol by the action of silver fluoride or mercurous fluoride on the iodo- or bromo-derivatives of the alcohols, and confirmed the observation of the Italian authors regarding the instability of the fluorides of the secondary alcohols. Further, Swarts tried to prepare a fluoride of fermentation amyl alcohol (mixture of 2-methylbutanol-1 and 3-methylbutanol-1) by the action of silver fluoride or mercurous fluoride on the iodo-derivative of fermentation amyl alcohol. The results were not satisfactory, as the impure fluorine compound partly decomposed on further fractionation, yielding small amounts of amylene. These results of Swarts were not encouraging, although the possibility existed that the fluoro derivative of 3-methylbutanol-1 was the unstable compound, whereas the fluoro derivative of 2-methylbutanol-1 could be stable. After several methods of fluorination had been tried out, it was found that the method of fluorination with silver fluoride, as given by Helferich and Gootz,[14] gave good results. They obtained β-fluorotetraacetylglucose by shaking at room temperature α-bromotetraacetylglucose with silver fluoride, using acetonitrile as a solvent in which silver fluoride is appreciably soluble. This modification of the fluorination with silver fluoride was successfully applied in the present investigation, as pure active 1-fluoro-2-methylbutane could be prepared. The method was used as follows: Commercial silver fluoride [15] was broken up in a mortar and thoroughly dried in a platinum dish in a vacuum desiccator over sodium hydroxide. Commercial acetonitrile was distilled a few times over phosphorus pentoxide and fractionated (boiling point, 83° C). As a platinum and a gold-palladium still-body of about 450 ml capacity each, and a gold-palladium receiver

[10] Compt. rend. **107**, 261 (1888).
[11] Compt. rend. **107**, 1155 (1888).
[12] Gaz. chim. Ital. **37II**, 309 (1907).
[13] Bul. acad. roy. Belg. [5] **7**, 438 (1921).
[14] Ber. deut. chem. Ges. **62B**, 2505 (1929).
[15] E. de Haen, Seelze (Hanover), Germany.

of about 300 ml were available, the procedure had to be repeated once for obtaining a sufficient amount of 1-fluoro-2-methylbutane. The amounts given below were worked up in one still-body.

Sixty g (49.5 ml) of pure *d*-rotatory-1-bromo-2-methylbutane (see below) with 60 g of silver fluoride and 240 ml of acetonitrile were shaken for 1 month at room temperature in a still-body, which was tightly closed with a rubber stopper. Every 3 days 1 g of silver fluoride was added, and every 7 days the rotation of the liquid was determined by filtering a small amount and making a reading with a tube 0.25 dm in length, the rotation remaining about the same after 3 weeks of shaking. After the shaking the liquid was allowed to stand undisturbed for 24 hours (reaction of the dissolved silver fluoride) and only the clear liquid was carefully decanted on a folded filter, keeping containers and funnel covered as much as possible, as the fluorine derivative is easily volatilized. The filtrate is distilled from a flask heated on a water bath, using a wide capillary and thermometer. The condenser and the ground-on receiver are cooled with ice water. The distillate up to 80° was collected and kept in a well-stoppered bottle. The residue in the flask was added to the wet residues in the platinum and palladium-gold containers, some acetonitrile added, and after 1 hour of shaking again allowed to settle and then decanted, distilling the filtrate as before. The two distillates were fractionated in small borosilicate glass fractionating columns until a constant-rotating material was obtained.

The smallest fractionating apparatus is constructed as follows (see fig. 1*b*): A flask 50 ml in capacity is sealed to a jacketed column with an inside diameter of 10 mm and a length of 350 mm, the jacket being evacuated. The flask has a side neck with ground-in capillary tube provided with a small stopcock for regulating the dry air current. The column tube is extended above the jacketed part to a length of about 250 mm in which the thermometer is suspended from a ground stopper. Parallel to this thermometer tube is the dephlegmator consisting of a tube 8 mm in diameter which is surrounded by a jacket 170 mm long for cooling with water or air. The dephlegmator is sealed at its lower end inside a wider tube, which, in turn, is sealed to the thermometer tube, thus allowing observation of the rate of reflux. At its upper end (where it is supported with a sealed-in glass rod by the thermometer tube) the dephlegmator is connected by a ground joint to the condenser. The filling consists of spiral rings made according to Wilson, Parker, and Laughlin.[16] The larger fractionating apparatus is constructed as follows: A flask 200 ml in capacity is sealed to a jacketed column, which has an inside diameter of 15 mm and is 500 mm in length. The apparatus is further constructed as described for the smaller one, the same filling being used. The ground connections of both columns fit into the ground part of the same condenser, which is, in turn, connected by ground joints to two test tube-shaped receivers in series, cooled by ice water contained in Thermos bottles, providing in this way facilities for vacuum fractionation, which is especially necessary for the bromo- and iodo-derivatives.

The fractionation of the fluoro-derivative is performed at ordinary pressure, cooling the condenser and receivers with ice water and heating with a small gas flame, the flask resting on an asbestos plate and surrounded by an asbestos box. By slow fractionation the liquid can

[16] J. Am. Chem. Soc. 55, 2795 (1933).

be separated in five parts, namely, first a small amount of low-boiling liquid having little optical activity, then three parts having increasing optical activity, and finally a residue of high-boiling impurities. Separate fractionations are then performed for the three main parts, the apparatus being always thoroughly cleaned and dried between distillations. Six fractionations had to be performed until a substance substantially homogeneous in boiling point and optical rotation was obtained. Many more fractionations were required for purifying the less pure fractions. A yield of the pure compound of 30 percent of the theory can be obtained. No further change in the recorded rotation could be observed by further fractionation. It will be noted that no chemical treatment is applied for obtaining the pure compound, which can be distilled without any decomposition.

Special methods had to be found for determining the fluorine, carbon, and hydrogen content of 1-fluoro-2-methylbutane, as this compound is very volatile.

The method used for determining fluorine is a combination of the one devised by Hahn and Reid [17] (who applied the Parr bomb for fluorine determinations) and that of Ost as applied by Helferich and Gootz,[18] who determined the fluorine by the loss of weight of a watch glass by etching. A specially constructed weighing tube made of steel is necessary (see fig. 1*g*). The tube is 25 mm high, has an inside diameter of 7 mm, a wall thickness of 1 mm, and has a well-fitted stopper. The flat bottom has a diameter of 15 mm, so as to make more difficult its upsetting. The description of a determination is as follows: 0.3 g of starch is carefully mixed with 15 g of sodium peroxide and kept in a closed bottle. The sample, 0.0813 g of 1-fluoro-2-methylbutane, is weighed off in the steel weighing tube and placed in the Parr bomb. The weighed sodium peroxide mixture is then added and the bomb closed. Without shaking, the bomb is ignited by a blast flame and kept hot for a few minutes, and then thoroughly cooled by running water for at least 10 minutes. The contents of the bomb are dissolved in water, filtered, neutralized with 10-percent hydrochloric acid, and made alkaline with sodium carbonate solution, as described by Hahn and Reid. The solution is concentrated by hanging the borosilicate glass beaker in the steam bath by means of a closely fitting copper ring, filtered from the silicic acid, the filtrate concentrated in the same manner to 100 ml, and 10 ml of 20-percent calcium chloride added drop by drop to the hot solution. The mixture is heated almost to boiling, making the precipitate granular, and cooled. The precipitate is filtered on a filter 7 cm in diameter. It is not necessary to wash the precipitate, and some of the precipitate may be left in the beaker. The filter with contents is dried and most of the contents shaken into the beaker, and the filter with the adhering precipitate is ashed in a platinum crucible. The crucible is rinsed with about 1.5 ml of glacial acetic acid and the solution stirred into the beaker, and 10 ml of water is used for cleaning the crucible and gradually added, with stirring, to the contents of the beaker. The contents of the beaker are evaporated by hanging the beaker in the steam bath, some water is added, and the evaporation repeated to remove all acetic acid. Five ml of water is added, the beaker is cooled and filtered on a filter 5.5 cm in diameter, using the filtrate over and over

[17] J. Am. Chem. Soc. **46**, 1652 (1924).
[18] Ber. deut. chem. Ges. **62B**, 2502 (1929).

again in order to bring all the precipitate of calcium fluoride on the filter. A few milliliters of water may be used in addition, but the precipitate is not washed. The filter is dried and ashed in a platinum crucible, which is fairly deep and has a sturdy, straight rim. Two watch glasses are weighed on an analytical balance and a few drops of 75-percent sulphuric acid are added to the contents of the crucible, which is directly covered with a tared watch glass. The crucible is heated in a sand bath for 2.5 hours at 150° C and then for a half hour at 200° C. The crucible is taken from the sand bath, cooled, the watch glass replaced by the second one, and the crucible again heated for a half hour at 200° C. The loss in weight of the cleaned watch glasses was found to be $0.0141+0.0003=0.0144$ g. A loss in weight of 0.00085 g corresponds to 0.001 g of fluorine. Fluorine found: 20.84 percent; theory: 21.09 percent.

In order to determine the carbon and hydrogen, the 1-fluoro-2-methylbutane was weighed into a specially constructed volatilizer (see fig. 1*e*) made of borosilicate glass. The rubber stopper of the combustion tube, having two holes of small diameter, is connected through one small tube directly to the dry oxygen and air supply; through the other hole the small tube of the volatilizer is introduced and the cork thoroughly fastened. The U-tube of the volatilizer is cooled in a beaker of ice water and cracked ice in order to prevent spreading of the volatile substance, and only at the end of the combustion is the ice water removed and heat applied to displace all the substance. With this arrangement the rate of delivery of vapor introduced into the combustion tube is easily controlled by regulating the oxygen stream through the volatilizer. Oxygen can also be introduced directly into the combustion tube through a by-pass. In the beginning combustions were made in a copper tube cooled at the end by copper spirals with running water for protecting the stoppers, the tube being filled with copper oxide and lead oxide (Moissan method)[19] or with the copper tube filled with copper oxide and lead chromate.[20] Both methods, however, were found unsatisfactory on account of the volatility of copper fluoride. Good results were obtained with a borosilicate glass tube filled with lead chromate and silver gauze, copper and copper compounds being excluded.[21]

The results of these analyses are: mass of substance, 0.1637 g; CO_2, 0.4009 g; H_2O, 0.1789 g. Calculated for $C_5H_{11}F$: C, 66.60; H, 12.31. Found: C, 66.79; H, 12.23.

(c) *d*-ROTATORY-1-CHLORO-2-METHYLBUTANE

The method of Le Bel for obtaining the chloro-derivative by heating a saturated solution of hydrochloric acid in active 2-methylbutanol-1 in sealed tubes at 100° C and further purifying by washing with water and sulphuric acid and sodium carbonate solution and finally fractionating, has been used by several investigators.[22] The products obtained by these investigators were not pure, probably on account of inadequate fractionation. This is essentially apparent for the product of Hardin and Sikorsky, who used only one distillation and one

[19] Compt. rend. **107**, 993 (1888).
[20] Schliemann and Pillarsky, Ber. deut. chem. Ges. **62**, 3035 (1929).
[21] Wallach and Heusler, Liebigs Ann. Chem. **243**, 243 (1888).
[22] Le Bel, Bul. assn. chim. [2] **21**, 542 (1874); [2] **25**, 545 (1876). Guye, Bul. soc. chim. [3] **25**, 547 (1901). Hardin and Sikorsky, J. chim. phys. **6**, 207 (1908).

fractionation and obtained a purity of 82 percent (taking a purity of 100 percent for the preparation of McKenzie and Clough, which is identical with the preparation obtained in this investigation).

In the preparation by Le Bel's process, the following procedure was used in the present investigation: 150 g of 98-percent *l*-rotatory-2-methylbutanol-1 was saturated at 0° C with hydrochloric acid and heated in sealed tubes in a steam bath for 5 hours. The reaction product was washed with water, dried with sodium sulphate, and fractionated in the fractionating columns used for the preparation of the active fluoro-derivative. By repeated fractionation, about 20 percent of the theoretical amount of pure active 1-chloro-2-methylbutane was separated and about 50 percent of active amyl alcohol recovered.

In the preparation by McKenzie and Clough's method [23] the following procedure was used: 20 g (24.5 ml) of 98-percent *l*-rotatory-2-methylbutanol-1 was gradually dropped from a burette in the course of a half hour through a condenser into a round flask, which contained 50 g (30 ml) of pure thionyl chloride. The flask was cooled in a dish with cracked ice. After addition of the 2-methylbutanol the mixture was kept at room temperature for 1 hour and then distilled in a vacuum of about 500-mm pressure, using a water pump and cooling the condenser and receiver with ice water. Fractionation gave about 28 g of dextrorotatory amyl chlorosulphinate with the properties described by McKenzie and Clough. In repeating the preparation several times with the double amount, the yield was somewhat diminished. The active amyl chlorosulphinate was converted to active amyl chloride according to McKenzie and Clough by refluxing for 2 hours at 120° C from an oil bath and fractionating the residue with the 500-mm column at ordinary pressure, cooling with ice water. The fractions with largest optical rotation were further fractionated, yielding a final product which did not change in boiling point or optical rotation upon subsequent fractionation and which was found to be identical in properties with the active amyl chloride by Le Bel's process.

(d) *d*-ROTATORY-1-BROMO-2-METHYLBUTANE

By the action of hydrobromic acid on pure *l*-rotatory-2-methylbutanol-1, Marckwald obtained a product which, on purification with sulphuric acid and fractionation, gave an active bromo-derivative with a specific rotation of $[\alpha]_D^{20}=+3.68$. Hardin and Sikorsky,[24] who started from 2-methylbutanol-1 of 92 to 95 percent purity (taking Marckwald's preparation as 100 percent), obtained, by the same procedure, for the bromo-derivative, $[\alpha]_D^{20}=+3.8$. Later Marckwald [25] applied the action of phosphorus tribromide on 2-methylbutanol-1 of 95 percent purity, and using the same method of purification, obtained for the specific rotation of the bromo-derivative, $[\alpha]_D^{20}=+4.05$. Marckwald remarked that on account of the presence of 5-percent isoamyl alcohol (which is inactive) in the starting material, the specific rotation of the pure bromo-derivative must be $+4.05+(5\times 0.04)=+4.25$. In the light of recent results the validity of this correction of Marckwald is questionable, as the impure bromo-derivative is treated with sulphuric acid, which besides eliminating the unchanged alcohol, may act also on the isoamyl bromide, which is less stable than the 2-methylbutanol derivative (see results of

[23] J. Chem. Soc. 103, 698 (1913). [24] J. chim. phys. 6, 207 (1908). [25] Ber. deut. chem. Ges. 42, 1583 (1909).
[24] J. chim. phys. 6, 207 (1908).
[25] Ber. deut. chem. 42, 1583 (1909).

Swarts on isoamyl fluoride). Further, the fractionation may also separate the different bromo-derivatives. Experimental evidence given below shows that both methods of bromination yield a product of identical specific rotation, which value agrees with the highest one actually found by Marckwald (+4.05).

In the preparation by the hydrobromic acid method the following procedure was employed: A special so-called double flask [26] (see fig. 1*d*), which can be used for saturating a liquid with a gas, as well as for drying a gas, was used for preparing the bromo- and iodo-derivatives. 60 g (73 ml) of 98-percent *l*-rotatory-2-methylbutanol-1 was cooled in ice in a double flask, which was connected at one end with a drying tube filled with asbestos and dry sodium sulphate, and connected at the other end with the hydrobromic acid generator. After saturation of the alcohol with hydrobromic acid, the double flask was connected with a reflux condenser having a drying tube at the upper end, and heated for 2½ hours in a water bath at 95° C, with a slow stream of hydrobromic acid passing through the liquid. The reaction product was cooled and separated from the watery layer in a separatory funnel, shaken two times with ice water, filtered clear through a dry filter, cooled in a dry separatory funnel, and shaken twice with about 8 ml of sulphuric acid which had been cooled with ice and salt, then with ice water, then with cold 10-percent sodium carbonate solution, and finally with ice water until a neutral preparation was obtained. Most of the water was removed by pouring the preparation from a dry Erlenmeyer flask. It was finally dried over potassium carbonate, and fractionated at 150-mm pressure, the condenser being cooled with ice water. The yield of the constant-boiling and rotating substance is about 70 percent of the theoretical. The preparation was repeated several times with slight variations but gave identical final products with properties recorded below.

In the preparation by the phosphorus tribromide method the following procedure was used: 80 g (28 ml) of phosphorus tribromide was slowly dropped through a condenser into 40 g (49 ml) of 98-percent *l*-rotatory-2-methylbutanol-1 contained in a flask cooled by ice. The condenser was sealed to the flask. A few "boiling" stones of unglazed porcelain were added. The mixture was allowed to stand overnight, the condenser being connected with an inverted calcium chloride tube. The next morning the flask was heated for about 10 minutes on the steam bath, the liquid turning turbid when the reaction started. The reaction product was cooled in ice and salt and poured on ice in a beaker which was cooled in an ice and salt mixture. The reaction product was separated from the watery layer in a separatory funnel and further purified as described for the method with hydrobromic acid. The preparation was repeated a few times, yielding identical final products.

(c) *d*-ROTATORY-1-IODO-2-METHYLBUTANE

This compound has been prepared by Klages and Sautter [27] and also by Marckwald,[28] applying the method of Just,[29] namely, heating a saturated solution of hydriodic acid in pure active 2-methylbutanol-1 at 100° C, purifying with cold dilute potassium hydroxide solution and ice water, drying over potassium carbonate, and fractionating.

[26] This device is not new, as it was used many years ago in a physical laboratory at Amsterdam. The advantage of this flask is that the liquid cannot be sucked into the gas generator by change of pressure.
[27] Ber. deut. chem. Ges. 37, 649 (1904).
[28] Ber. deut. chem. Ges. 37, 1038 (1904).
[29] Liebigs Ann. Chem. 226, 149 (1883).

The specific rotation found by these authors is identical with that found in the present investigation. It was found, as described below, that the iodo-compound can be prepared by heating at 60 to 65° C, instead of 100°.

In the present investigation the following procedure was used: 40 g (49 ml) of 98-percent *l*-rotatory-2-methylbutanol-1 was cooled in ice in a double flask (see under 1-bromo-2-methylbutane), which was connected at one end with a drying tube filled with asbestos and dry sodium sulphate and connected at the other end to the hydriodic acid generator. After saturation of the active alcohol with pure dry hydriodic acid at 0°, the flask was heated in a water bath for 1 hour at 60 to 65° C, with a slow stream of hydriodic acid passing through the liquid. The reaction product was cooled and separated from the top watery layer in a separatory funnel, shaken once with 10 ml of ice water, then with 15 ml of cold 10-percent sodium hydroxide solution until acidity was removed, and finally with ice water until a neutral preparation was obtained. Most of the water was removed by pouring the preparation from a dry Erlenmeyer flask. It was finally dried over potassium carbonate, and fractionated at 50-mm pressure, the condenser and receiver being cooled with ice water. The yield of the "constantly boiling" and "constantly rotating" substance is about 65 percent.

2. PROPERTIES OF PURE COMPOUNDS

(a) OPTICAL ROTATION

The optical rotation was determined with a polariscope with circular scale and double-field Lippich polarizer. Jacketed glass polariscope tubes were used, which were checked for the recorded length. For each pure compound investigated, the rotation was determined for the two wave lengths, 5892.5 and 5461 A, on the circular-scale polariscope, using spectrally purified light from an electric sodium lamp and an electric mercury lamp, respectively. A third determination was made, using the same sample and tube with the Bates saccharimeter, and using white light and a bichromate filter, which gives an effective wave length of about 5850 A. These data are given in table 1, together with values reported by Marckwald and McKenzie,[30] McKenzie and Clough,[31] and Klages and Sautter.[32] The data of the many other investigators who prepared optically active 2-methylbutanol-1 and its derivatives are not included because their compounds were very impure.

(b) SPECIFIC GRAVITY

No concordant results were obtained with picnometers in which the liquid is in contact with ground joints. Picnometers of 5 and 10 ml capacity, with ground caps were constructed and served well for the purpose (see fig. 1). The liquid level was conveniently adjusted by the use of strips of hardened filter paper, and the loss of liquid by evaporation was prevented by the cap. The picnometer was filled and emptied by using a pipette with a capillary stem. The specific gravity was determined with the picnometer at 20° C, and a formula applied for obtaining the specific gravity at 20°/4° in vacuo. These data, together with those of some earlier investigators, are given in table 1.

[30] Compt. rend. 41, 296 (1873).
[31] Ber. deut. chem. Ges. 37, 649 (1904).
[32] Compt. rend. 107, 1155 (1888).

TABLE 1.—*Optical rotation, specific gravity, and refraction of 1-halogeno-2-methylbutanes*

TABLE 1.—*Optical rotation, specific gravity, and refraction of 1-halogeno-2-methylbutanes*

Substance	Optical rotation: Observed rotation α for: λ5892.5 A	λ5461 A	White light and bichromate filter	Optical rotation: Specific rotation $\frac{\alpha}{ld}$ for: λ5892.5 A	λ5461 A	White light and bichromate filter (5850 A at 20° C)	Optical rotation: Specific rotation reported by other investigators	Specific gravity: d^{20}_4 vac.	Specific gravity: d By other investigators	Refractivity: Refractive index n^{20}_D	Refractivity: Molecular refraction $M\frac{n^2-1}{(n^2+1)d}$
l-Rotatory-2-methylbutanol-1.	−9.432 (2 dm)*	−11.200 (2 dm)	−9.47 (2 dm)	−5.756 (at 20.4° C)	−6.835 (at 20.4° C)	−5.78	$[\alpha]_{88}{}^{20}{}_{32}=-5.90$ (Marckwald and McKenzie.)	0.8193	$d^{20}_4=0.816$ (Marckwald and McKenzie.)	1.4107	35.605
l-Rotatory-1-fluoro-2-methylbutane.	−7.009 (1 dm)	−8.283 (1 dm)	−7.01 (1 dm)	−8.865 (at 20.1° C)	−10.477 (at 20.1° C)	−8.87		.7906		1.3576	24.997
d-Rotatory-1-chloro-2-methylbutane.	+1.456 (1 dm)	+1.636 (1 dm)	+1.49 (1 dm)	+1.644 (at 20.1° C)	+1.847 (at 20.3° C)	+1.68	$[\alpha]^{18}{}_D=+1.7$ (McKenzie and Clough.)	.8857	$d^{18}_4=0.8868$ (McKenzie and Clough.)	1.4124	29.957
d-Rotatory-1-bromo-2-methylbutane.	+4.946 (1 dm)	+5.758 (1 dm)	+5.00 (1 dm)	+4.043 (at 20.6° C)	+4.707 (at 20.6° C)	+4.09	$[\alpha]^{20}{}_D=+4.05$ (Marckwald.)	1.2234		1.4451	33.512
d-Rotatory-1-iodo-2-methylbutane.	+8.672 (1 dm)	+10.107 (1 dm)	+8.71 (1 dm)	+5.685 (at 19.8° C)	+6.626 (at 19.8° C)	+5.71	$[\alpha]^{18}{}_D=+5.78$ (Klages and Sautter.) $[\alpha]^{20}{}_D=+5.64$ (Marckwald.)	1.5253	$d^{20}_4=1.524$ (Marckwald.)	1.4977	38.033

* Length of tube.

(c) REFRACTIVE INDEX

The values of refractive index were determined with an Abbe refractometer at 20° C. These data, together with calculated values of the molecular refraction, are given in table 1.

(d) BOILING POINTS AT VARIOUS PRESSURES

A Cottrell-Washburn boiling-point apparatus [33] was used with some modifications (see fig. 1*c*): The withdrawal tube was omitted. The boiling tube is sealed to the condenser and is constricted at the bottom. This constricted part is 60 mm long and 15 mm in diameter and has a flat bottom. The upper part of the boiling tube is 200 mm long and is 40 mm in diameter. The glass sheath, which is ground into the boiling tube, has at its top, just above the ground connection, a ground stopper with an eye from which a short accurately standardized thermometer, graduated in 0.2° C intervals, is suspended by a platinum wire. The glass sheath, 28 mm in diameter, extends slightly above the constriction of the boiling tube, and has a hole 6 mm in diameter at the height at which the condenser is sealed on. The pumping tubes, 3 mm in diameter, are attached from their top to the inside of the sheath, the holes being about 28 mm above the end of the sheath and about 10 mm apart. The pumping tube is widened at its lower end to a funnel 8 mm wide extending to near the bottom of the boiling tube. Inverted melting-point tubes or small pieces of unglazed porcelain were used for preventing bumping. These modifications allowed the use of small amounts of liquid for the determination. For low pressures the reflux condenser was cooled with ice water, which could be kept running without a pump by slowly siphoning water through the condenser from the bottom of a large crock filled with big chunks of ice, which was kept filled at a constant level by tap water. The pressure of the boiling liquid was maintained within fluctuations of about 0.1 mm of Hg by increasing the volume at constant pressure to about 5 liters. Calibration corrections were applied to the thermometer readings. The values of the boiling points correspond to the given pressures in terms of millimeters of Hg at 0° C and standard gravity (g=980.665). The results are compiled in table 2, and shown graphically in figure 2.

TABLE 2.—*Boiling points*

Pressure	*l*-Rotatory-2-methylbutanol-1	*l*-Rotatory-1-fluoro-2-methylbutane	*d*-Rotatory-1-chloro-2-methylbutane	*d*-Rotatory-1-bromo-2-methylbutane	*d*-Rotatory-1-iodo-2-methylbutane
mm of Hg	°C	°C	°C	°C	°C
50	65.7		27.7	45.0	66.5
100	79.6		43.0	61.4	84.1
150	88.2	14.1	53.1	71.7	95.4
200	94.6	20.7	60.4	79.5	103.5
300	104.1	30.4	71.5	91.1	115.7
400	111.4	37.8	80.0	100.1	125.3
500	117.3	43.7	86.8	107.4	132.6
745[a]		55.4			
747[a]	128.6				
758[a]	128.7	55.85	100.2	121.5	
763.6[a]			100.7		
760[b]	128.9	55.9	100.45	121.6	[c]

[a] Atmospheric pressure, observed.
[b] Values calculated to normal boiling point.
[c] Decomposed.

[33] J. Am. Chem. Soc. 41, 730 (1919).

III. DISCUSSION OF RESULTS

The similar procedure used for preparing the chlorine, bromine, and iodine derivatives makes it very probable that these derivatives are of the same configurational form, whether or not a Walden inversion is involved in their preparation. It is immaterial for our present purpose whether this form fits into any particular scheme of classification as a *d*-form or as an *l*-form, and it will be noticed that we have described the compounds as *d-rotatory*. In the case of the fluorine compound, however, it is not certain whether the *negatively* rotating form must be classified with the other halogen derivatives which are positively rotating (possibility 1) or whether the positively rotating form must be taken (possibility 2).

TABLE 3.—*Comparison of the numerical relation* (Cl–F):(Br–Cl):(I–Br) *of the molecular rotations of 1–halogeno–2–methylbutanes for 5892.5* A *and for 5461* A *at 20°* C *with the numerical relation of the atomic-radii differences between the respective halogens*

Explanation of table.—The values given in column 5 have been obtained by multiplying the values of column 3 by a factor, which will reduce the first value to 41. This value has been chosen in order to conform to the values given in column 4 for the numerical relation between the differences of neutral atomic radii.

1	2	3	4	5
Compounds	Molecular rotation in circular degrees	Differences between molecular rotations	Relation of the differences between atomic radii in angstroms	Reduced relation of the differences between molecular rotations
	For λ 5892.5 A:			
F	−799.1			
Cl	+179.0	978.1	0.41	0.41
Br	+610.1	431.1	.16	.181
I	+1124.7	514.6	.21	.216
	For λ 5461 A:			
F	−943.8			
Cl	+196.8	1140.6	.41	.41
Br	+710.8	514.0	.16	.185
I	+1312.0	601.2	.21	.216

In table 3 the first possibility is tested for the atomic-dimension relationship and it will be seen that the numerical relationship of (Cl–F):(Br–Cl):(I–Br) of the molecular rotations is 41:18.1:21.6 for 5892.5 A, and 41:18.5:21.6 for 5461 A, which agrees well with the numerical relationship of the successive differences in the radii of the neutral halogen atoms, 41:16:21. These differences (Cl–F), (Br–Cl), and (I–Br) are obtained by averaging the ratio of the differences in the radii given by van Arkel and de Boer and the ratio of the differences derived from the values given by Goldschmidt.[34] Probably the numerical relationship of these differences of atomic radii is most accurately represented by 41:17.1:21.4, as suggested by the author,[35] which shows even a closer agreement with the observed numerical relationship. It is further noteworthy that in spite of the very different values of the rotations for the two wave lengths, the ratio of their differences is the same.

[34] BS J. Research **7**, 573 (1931) RP 358.
[35] J. Am. Chem. Soc. **47**, 1285 (1925); BS J. Research **7**, 573 (1931) RP358.

For the second possibility no apparent regularity is obtained (if the positively rotating fluorine derivative is included). This will be observed from the rotations given which, with the positively rotating fluorine derivative, show first a decrease and then an increase in value for both the specific and the molecular rotation. Thus the above reasoning classifies the *positively* rotating chlorine, bromine, and iodine derivatives with the *negatively* rotating fluorine derivative. This appears strange. However, we arrive at the same conclusion by taking into consideration that it is very improbable that in any of the reactions used for preparing the halides a Walden inversion is involved, as the reactions take place at inactive carbon atom, and temperatures (at most 100°) are applied for which no racemization of the alcohol or the halides can be observed.[36] Further, it is obvious from these data that the differences in weight of the four groups attached to the asymmetric carbon atom (Guye's hypothesis) cannot be used for correlating the rotations in both possibilities, as theory would require for the differences in rotation (Cl–F):(Br–Cl):(I–Br) the proportionality 16.5:44.4:47.0. This differs greatly from the observed data.

The reduced differences in the boiling points at the same pressure of the (Br–Cl) and (I–Br) derivatives have a numerical relationship which agrees with that for the differences in atomic radii of the respective neutral atoms, whereas a deviation for the (Cl–F) difference exists. In table 4 the reduced ratio for one pressure is given, the ratio for other pressures being substantially the same. This behavior is not unexpected, as such restricted relationship has been pointed out and discussed by the author for the elements F, Cl, Br, and I in a former publication.[37]

TABLE 4.—*Comparison of boiling points at equal pressure of 1–halogeno–2–methylbutanes with the differences in the atomic radii of halogens*

The values given in column 3 have been obtained by multiplying the values of column 2 by a factor, which will reduce the second value to 16. This value has been chosen in order to conform to the values given in column 4 for the numerical relation between the differences in the radii of neutral atoms (Br–Cl):(I–Br), 16:21. There is a deviation of the (Cl–F) value. Closer agreement is obtained by comparing with the numerical relation of the atomic radii as observed by the author (J. Am. Chem. Soc. 47, 1280 (1925)) 41:17.1:21.4, the reduced numerical relation of the boiling-point differences for 150 mm Hg then being 35.8:17.1:21.8.

1	2	3	4
Pressure	Numerical relation between boiling-point differences (Cl–F):(Br–Cl):(I–Br)	Reduced numerical relation between boiling-point differences (Cl–F):(Br–Cl):(I–Br)	Numerical relation between differences in radii of neutral atoms (Cl–F):(Br–Cl):(I–Br)
150 mm of Hg	39.0:18.6:23.7	33.5:16:20.4	41:16:21

[36] Marchwald and Nolda (Ber. deut. chem. ges. *42*, 1591 (1909)) investigating the possibility of a Walden inversion also came to the conclusion that the negatively rotating 2-methyl butanol-1 and the positively rotating bromine and iodine derivatives are of the same configuration. The writer does not agree however, with Marchwald's and Nolda's generalisation that a racemic influence is due to silver salts. This will be discussed in a later paper.

[37] NBS J. Research 17, 337 (1936) RP915. The same regularity holds for the molecular refractivities and the cube roots of the molecular volumes according to Kopp.

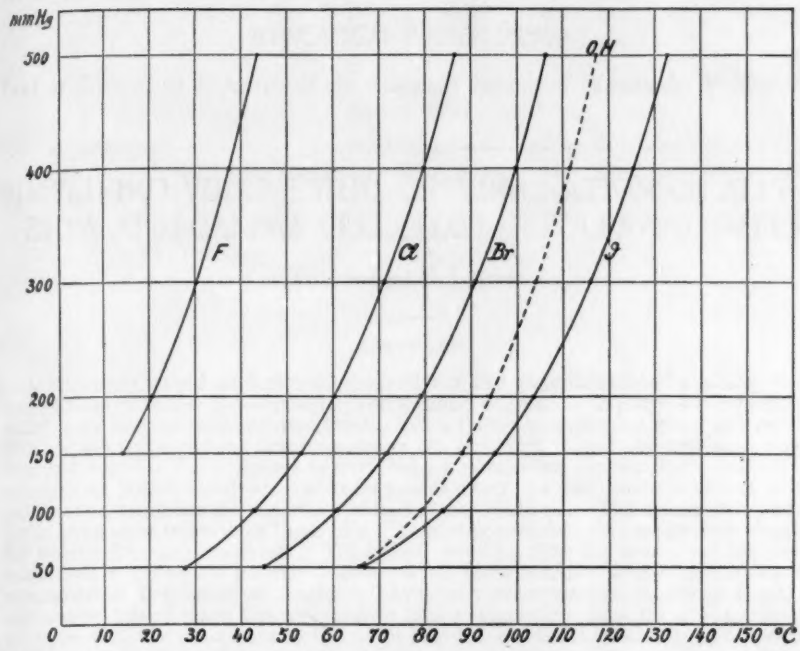

FIGURE 2.—*Boiling-point curves for l-rotatory-2-methylbutanol-1 and its halides.*

IV. CONCLUSIONS

The results of this investigation show that the differences in the molecular rotations (Cl–F), (Br–Cl), and (I–Br) of the four pure active halogeno–2–methylbutanes have the numerical relation 41:18:21.6 (for λ 5892.5 A, as well as for λ 5461 A), which agrees well with the numerical relation 41:16:21 for the differences in the radii of the respective neutral atoms. As the halogens of these simple compounds are attached *indirectly* (by a chain of atoms) to the asymmetric carbon, these results support the rule proposed by the author [38] for this class of compounds for the more complicated carbohydrate derivatives.

The other crucial test for that part of the regularity which applies to halogen derivatives in which the halogen is *directly* attached to the asymmetric carbon, and contains only one asymmetric carbon atom, and which involves the specific rotation, will be given in a forthcoming publication.

WASHINGTON, January 18, 1937.

[38] J. Am. Chem. Soc. 47, 1285 (1925).

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SIMPLIFIED VOLUMETRIC DETERMINATION OF ALPHA, BETA, AND GAMMA CELLULOSE IN PULPS AND PAPERS

By Herbert F. Launer

ABSTRACT

A relatively rapid and simple method for the determination of alpha, beta, and gamma cellulose is described. The method ordinarily employs a 0.3-g sample, which need not be weighed accurately, but a 0.03-g sample also gives fair results. Neither ash nor moisture determinations are involved, in fact, no precision weighings are made. The cellulose is oxidized by potassium dichromate solution, the strength of which need not be known accurately, as the concentrations of the oxidimetric solutions do not enter into the calculations. The volumetric results are in good agreement with those of a gravimetric method, and are as reproducible, for widely different materials. The actual working time for four complete determinations is 1½ to 2½ hours. Fundamental facts recently found concerning the separation of the cellulose fractions have been incorporated in the method. A calculation based upon the volumetric and gravimetric data for alpha cellulose indicates that the pentosans in the pulps studied are distributed among the alkali-soluble and alkali-insoluble fractions in approximately the same ratio as cellulose. It was also found that the amount of beta cellulose which precipitates is dependent upon the temperature, and that the separation should be made without heating the acidified filtrate.

CONTENTS

	Page
I. Introduction	333
II. Method in detail	336
1. Mercerization and filtration	336
2. Treatment of alpha cellulose	336
3. Treatment of the filtrate	337
(a) Beta plus gamma portion	337
(b) Gamma portion	337
III. Treatment of the values obtained	337
1. Calculation of the percentages of alpha, beta, and gamma cellulose	337
2. Calculation of the total cellulose content of the sample	338
IV. Experimental results and discussion	339
1. Volumetric values for alpha cellulose compared with the gravimetric results	339
2. Volumetric results for beta and gamma cellulose	341

I. INTRODUCTION

Cellulose consists analytically of three fractions, alpha, beta, and gamma, which terms have been defined frequently in the literature.[1 2 3 4 5 6 7]

[1] Jentgen, also Bubeck. See Schwalbe, Papier-Fabr. 26, 196 (1928), for these and further references.
[2] Burton and Rasch, BS J. Research 6, 603 (April 1931) RP295. See also TAPPI tentative standard T429m, Alpha Cellulose in Paper, also T203m, Alpha Cellulose in Pulp.
[3] Ritter, Ind. Eng. Chem., Anal. Ed. 1, 52–4 (1929).
[4] Bray and Andrews, Ind. Eng. Chem., 15, 377 (1923). See discussion also in Hawley and Wise, The Chemistry of Wood, p. 144–148 (Chemical Catalog Co., Inc., New York, N. Y.)
[5] Lewis and Browning, Paper Trade J. 97, 39 (Dec. 1933).
[6] Methods used at the U. S. Forest Prod. Lab., Compiled by Bray, Paper Trade J. 87, no. 25, 63–4 (Dec. 20, 1928).
[7] Porrvik, Papier-Fabr. 26, 81 (1928).

The alpha fraction is the cellulose which can be filtered from a mixture consisting of sodium hydroxide solution and the material being analyzed. Further differentiation is obtained by acidification of the filtrate, whereupon the beta fraction precipitates, and the gamma fraction remains in solution. Such a definition is dependent upon the factors involved in the separation, such as amount and concentration of the sodium hydroxide solution, the physical state of the fibers, such as freeness and extent of fibrillation, the time of contact between solution and fibers, and the method of filtering and washing. Thus, the values obtained for the cellulose fractions depend upon the particular method used, although the values found in the literature for certain well-known materials differ by only 1 to 2 percent.

A high content of alpha cellulose usually indicates good quality, as for example, stability of the finished material, other things being equal. The interest in beta and gamma cellulose seems to be solely academic. The correlation between the quality of the cellulose product and the alpha-cellulose content is, however, not close enough to indicate which of the existing methods yields the most useful values. Furthermore, the experiments of Porrvik [8] and of Lewis and Browning indicate that alpha cellulose will dissolve indefinitely if treated with fresh portions of sodium hydroxide solutions. Apparently no practicable method for routine and control work can yield a value which is a fundamental constant for a given material.

It seems, therefore, that the only criteria for the suitability of a given method are its simplicity and rapidity of execution, and its reproducibility, not only as regards agreement between duplicate determinations, but also as regards comparison between various papers among themselves, or with the original pulp. It frequently happens that a pulp may be filtered in 5 to 30 minutes, whereas a paper made from the pulp may require 3 to 5 times as long, sometimes 3 to 4 hours in extreme cases. The corresponding alpha-cellulose values obtained by commonly used methods would not be comparable for such a case, for, as Porrvik and Lewis and Browning have shown, large differences (2 percent, within a given method) in alpha-cellulose content may arise from variations in the rates of filtration, unless the cellulose-alkali mixture is allowed to stand a certain length of time after dilution. The rate of filtration appears to have very little effect if the mixture is filtered 1 hour or more after dilution. It appears that all the reactions between cellulose and alkali should be given a sufficient length of time to reach equilibrium. This applies to the washing as well as to the mercerization.

The alternative of allowing a reaction to reach equilibrium in order to achieve reproducibility is to allow the reaction to proceed for a definite length of time. The Faserstoff-Analysenkommission [9] specify exactly 5 minutes for washing the alpha cellulose with a definite quantity of 8-percent alkali. This is impossible to regulate in the case of paper, which fact is tacitly recognized by them, since they consider their method to be applicable only to pulps.

At the National Bureau of Standards it was necessary to develop a method which would be valid for the analysis not only of pulps but also of the papers usually causing difficulties in filtering. Special

[8] See footnotes 5 and 7.

[9] Faserstoff-Analysenkommission des Vereins der Zellstoff und Papier-Chemiker und -Ingenieure, Papier Fabr. 32, 521 (1934).

attention was paid to the aspects of simplicity, rapidity of operation, and reproducibility, especially of the type mentioned. The mercerizing procedure of Lewis and Browning was adopted, including observance of the time necessary to reach equilibrium in the swelling in 17.5-percent, and subsequent standing in the diluted (7.3-percent) alkali. The alpha cellulose was washed with water only.[10] In this way, any uncertainties arising from variations in the rate of washing with sodium hydroxide solutions are avoided. Furthermore, the ratio of the volume of alkali to the weight of sample has been made unusually large to minimize errors due to "drop losses."

The method described in the present article is based entirely upon volumetric procedures. It is simple and rapid, since no precision weighings are involved, and since the sample taken for analysis is small, 0.3-g. Moisture and ash determinations on the ground material, indispensable in other methods, are not made. The entire alpha-cellulose portion, and large aliquot parts of the filtrate, one-half and one-quarter, for the beta plus gamma, and gamma portions, respectively, are oxidized with dichromate solution, the strength of which need not be known accurately. The method, using a 0.3-g sample, is shown to be equal in precision to gravimetric methods employing much larger samples. Even a 0.03-g sample was found to yield fair results. Aside from the obvious advantages of a precision method which is applicable when only small samples are available, the use of a small sample has the advantage that the entire separation even in the worst cases requires less than one-half hour. The 3- to 5-g samples ordinarily employed require up to 3 or 4 hours in such cases. For most pulps, eight complete separations of the alpha from the soluble cellulose can usually be made per hour with the method described in this article. For most papers, the corresponding number per hour is six to seven. Thus, four complete determinations of alpha, beta, and gamma cellulose require an actual working time of 1½ to 2½ hours, which is about one-eighth to one-fourth of the time necessary for the same number of determinations by any other method.

Bray and Andrews,[11] who adapted Bronnert's[12] method for determining alkali-soluble cellulose with dichromate to the alpha, beta, and gamma cellulose determination, discuss further advantages inherent in volumetric methods. Their procedure involves, however, the usual moisture and ash determinations, and recommends the standardization of the potassium dichromate solution against "Cross and Bevan cellulose" from sulfite pulp. They limit their comparison of the volumetric and gravimetric results to a study of spruce sulfite pulp. However, their method of filtration is not suitable for paper analyses and they take one-tenth and one twenty-fifth aliquot parts for the alpha, beta plus gamma, and also gamma fractions, respectively, whereby errors in the dichromate determinations are multiplied by 10 and 25.

Porrvik[13] uses a volumetric method which is peculiarly adapted to the needs of the rayon industry. In this method only a partial (5/8) separation of alpha from beta and gamma cellulose is attempted, and

[10] Thirty-five milliliters of water is sufficient. It was found that further washing extracts no more cellulose.

[11] Bray and Andrews, Ind. Eng. Chem. **15**, 377 (1923). See discussion also in Hawley and Wise, The Chemistry of Wood, p. 144-148. Chemical Catalog Co., New York, N. Y.). The method is quite similar to that of the Faserstoff-Analysenkommission (footnote 9).

[12] In Schriften des Vereins der Zellstoff und Papier-Chemiker **13**. Die chemische Untersuchung pflanzlicher Rohstoffe und der daraus abgeschiedenen Zellstoff, compiled by C. G. Schwalbe. Published by Verlag der Papier-Zeitung, C. Hofmann, Berlin (1920). It is a report on the secret process of the Bayerische Glanzstoffwerke, and is very incomplete.

[13] Porrvik, Papier-Fabr. **26**, 81 (1928).

very small aliquot parts, 1/120 and 1/150, for the alpha and gamma portions, respectively, are taken. Furthermore, Porrvik works only with bleached sulfite pulp and makes no comparison with the results of a gravimetric method for alpha cellulose.

The gravimetric methods [14] include for duplicate determinations, 22 precision weighings, including 12 for moisture and ash; 6 more are necessary if beta cellulose is to be determined.

The materials studied in this work were soda pulp, refined sulfite and sulfate pulps, known on the market as "alpha" pulp and bleached sulfate, respectively, also no. 1 old white rags, no. 1 new white rags, and no. 1 new white rag paper. The resins in these materials did not in any case exceed 0.2 percent, and were neglected. It will be shown in a later paper that this has no effect upon the results and also that a correction may be applied for larger amounts of resin.

II. METHOD IN DETAIL

1. MERCERIZATION AND FILTRATION

Approximately 0.3–g of the material reduced to fibrous condition in a "Dr. Koerner-type" grinder and well-mixed [15] is weighed in a 100-ml beaker to the nearest 10 mg. 20.0 ml of 17.5-percent [16] sodium hydroxide solution is added to the sample, which is then macerated until uniformly wet and dispersed, and allowed to stand for 10 minutes. 33.0 ml of water is then added, the mixture thoroughly stirred, and allowed to stand for 1 hour, stirring once during the interval. After stirring once more, about 5 ml of the unsettled mixture is poured into a Gooch crucible and allowed to drain without suction. The filtrate and wash water run directly into a 100-ml volumetric flask. With very gentle suction (pressure differential 10 to 20 mm of Hg) the mat is formed through which the rest of the mixture is filtered. By avoiding excessive packing of the fibers owing to strong suction, very rapid filtering is usually secured. If the mat was successfully formed at the outset the filtrate is poured back through it only once. The mat without being broken up is then washed with 35 ml of water. The filtrate is diluted to the mark and treated as described later in section 3. The alkali-cellulose mixture, as well as the water and sodium hydroxide solution, are kept at $20.0 \pm 0.1°$ C.

2. TREATMENT OF THE ALPHA CELLULOSE

The alpha cellulose is moistened and removed from the crucible. The crucible is placed upright in a 400-ml beaker and filled with 25 ml of 12*M* (approximately 75-percent, by weight) sulfuric acid, at room temperature, and then rinsed after a few minutes with 50 ml more of the acid. The alpha-cellulose pad is then disintegrated in the acid using a thermometer as stirring rod. After the alpha cellulose has dissolved, 25.00 ml of potassium dichromate solution [17] is added. The

[14] See footnotes 1, 2, 3, 5, and 6.

[15] The use of a small sample requires that the material be well mixed after grinding. This can readily be accomplished by such an apparatus as is described by Lewis and Browning. The present writer used an upturned bell jar, 30 cm diameter by 22 cm depth, upon which fits a heavy wooden lid, carrying a small motor and fan. By the proper placing of a vane to produce cross currents, the mixing of 40 g of material in 20 min was found to produce a sufficiently homogeneous sample, as the chemical tests showed.

[16] Made by diluting the 50-percent solution, from which the sodium carbonate has been allowed to settle, to 5.22*N*, when titrated with standard acid using phenolphthalein. An excess of barium chloride is added at the beginning of the titration to remove carbonate from solution.

[17] The solution is made up directly from oven-dry (100 to 110° C) $K_2Cr_2O_7$ by dissolving 90.00 g in water at 70 to 90° C, allowing to cool to 20° C, and diluting to 1 liter. Its calculated normality is 1.835, but one of the advantages of the present method is that an exact knowledge of the strength of any of the oxidimetric solutions is not necessary.

solution is heated to 140 to 150° C, at which temperature it is maintained for approximately 10 minutes. Air is constantly bubbled in a fine stream through the solution to prevent troublesome bumping. The breaker should be covered with a watch-glass cut or notched to permit entrance of the thermometer and bubbling tube.

After the solution has cooled to 130 to 140° C, 50 ml of water is added, the thermometer, etc., are rinsed down, and the solution cooled to 60° C or lower. The remaining dichromate is then most simply titrated electrometrically [18] with 0.5*M* ferrous ammonium sulfate solution.[19]

3. TREATMENT OF THE FILTRATE

(a) BETA PLUS GAMMA PORTION

50.00 ml of the filtrate is pipetted into a 400-ml beaker containing 5.00 ml of the potassium dichromate solution. Cautiously, and with constant stirring, 50 ml of concentrated sulfuric acid is slowly poured down the side of the beaker. The solution is then heated and later titrated as in part 2.

(b) GAMMA PORTION

The pipette used to deliver the beta plus gamma portion is rinsed out into the remaining filtrate, which is then acidified with 15 to 16 ml of 6.0*N* sulfuric acid, using no indicator. After cooling, the cloudy mixture is diluted to 100 ml, poured into a Nessler tube or graduate cylinder and allowed to stand overnight. After the beta cellulose has settled, a 50.00-ml portion of the supernatant liquid is cautiously removed and treated exactly as noted in part (a). The beta plus gamma mixture should be at room temperature while the gamma portion is removed.

III. TREATMENT OF THE VALUES OBTAINED

1. CALCULATION OF THE PERCENTAGES OF ALPHA, BETA, AND GAMMA CELLULOSE

The percentage of each fraction of cellulose is calculated by dividing the volume of dichromate corresponding to it by the total volume of dichromate for all three fractions. For example, if the alpha cellulose used 18.48 ml, and the beta plus gamma cellulose used 3.48 ml of dichromate, then the total cellulose dichromate value is 21.96 ml, and the alpha-cellulose content [20] is

$$\frac{18.48}{18.48+3.48}\times 100 = 83.8\%.$$

The gamma-cellulose content is calculated in a like manner. The beta-cellulose content is found by difference.

[18] A relatively inexpensive galvanometer with a sensitivity of 0.5 to 1 microampere per millimeter scale division, used in circuit with an ordinary sliding-contact rheostat, platinum electrode and calomel half-cell will suffice. The same titration may also be carried out, however, less rapidly, using potassium ferricyanide as outside indicator, in which case, 400, rather than 50, ml of water is added before titrating the dichromate in the alpha-cellulose determinations.

[19] Contains 195 g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ and 10 ml of concentrated H_2SO_4 per liter. If the solution is kept out of contact with oxygen its strength remains fairly constant.

[20] These as well as all corresponding figures have been corrected for the sulfuric acid blank, which is usually 0.01 to 0.02 ml of dichromate per 50 ml of sulfuric acid. This is determined under typical test conditions.

2. CALCULATION OF THE TOTAL CELLULOSE CONTENT OF THE SAMPLE

A knowledge of the total cellulose content of the ground material, although not involved in this method for determining alpha, beta, and gamma cellulose, is necessary for use in other chemical tests, such as copper number, pentosans, etc. If these tests are to be made, the sample for the determination of alpha, beta, and gamma cellulose is weighed to the nearest 1 to 2 mg instead of 10 mg. From this weight and from the volume of dichromate for total cellulose, the total cellulose content may be calculated.

For this calculation the equivalent weight of cellulose, $C_6H_{10}O_5$, is taken to be 162.1/24=6.75 g. From this and from the strength of the dichromate solution, 1.835*N*, it is calculated that 1 ml of dichromate solution will oxidize 0.0124 g of cellulose. From the weight of the sample taken for the determination of alpha cellulose 0.300 g, and the volume of dichromate for total cellulose,[21] 21.96 ml, for example, the total cellulose content of the sample is

$$\frac{21.96\times 0.0124}{0.300}\times 100=90.8 \text{ percent.}$$

The values so calculated are listed in table 1 as total cellulose content (volumetric), and may be compared with the values of total cellulose content (gravimetric). The latter were obtained by determining gravimetrically the moisture and ash content, using standard procedures, and assuming the remainder of the material to be cellulose.[22]

The values for the total cellulose content (volumetric) are sufficiently accurate [23] for the purpose stated.

The elimination of the moisture and ash determinations on the ground sample constitutes a substantial saving of time in routine control and even research work.

TABLE 1.—*Comparison of the two methods for obtaining the total cellulose content of pulps and papers*

Method	Materials					
	• 1035 (no. 1 new white rag paper)	1009 (no. 1 old white rags)	1039 (refined sulfate pulp)	1018 (soda pulp)	988 (refined sulfite pulp)	1008 (no. 1 new white rags)
Total cellulose content, gravimetric (%)	84.96	93.38	91.25	91.86	92.27	93.12
Total cellulose content, volumetric (%)	84.3	93.4	90.8	91.4	91.6	92.8

• The numbers are those used in connection with other experiments. See Shaw and O'Leary, *Study of the effect of fiber components on the stability of book papers.* J. Research NBS **17**, 859 (1936) RP949.

[21] Total cellulose dichromate values are given in table 2, column 5.

[22] The values so obtained are used directly in the copper-number determination, wherein no attempt is made to distinguish pentosans from cellulose. The corrections for resin, etc., are negligible for the materials listed but may be made when significant, as will be shown in a later paper.

[23] The greatest disagreement between volumetric and gravimetric values in table 1 is 0.7 percent and the average is 0.4 percent. The standard method for the determination of copper number in paper, TAPPI tentative standard, T430m, specifies an agreement between duplicates of 0.1 copper-number unit. This corresponds to 2.5 percent for even relatively high copper numbers of 4.0.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

1. VOLUMETRIC VALUES FOR ALPHA CELLULOSE COMPARED WITH THE GRAVIMETRIC RESULTS

The validity of a volumetric method is usually determined by a comparison with the results of a gravimetric method. Accordingly, a 1-g sample of each material studied was subjected to the same treatment as the 0.3-g sample for the separation of the cellulose fractions. The same ratio of alkali volume to weight of sample, was, of course, maintained. The alpha cellulose was filtered in a Gooch crucible provided in this case with a small piece of cotton cloth as filtering medium. The residue was first washed with 100 ml of water, allowed to soak for 10 minutes in 20-percent acetic acid, and finally washed with 500 cc of water, the pad being constantly broken up with a pointed stirring rod. It was then dried, weighed, and ignited as usual. The alpha-cellulose values were calculated on the basis of the oven-dry ground sample, corrected likewise for ash.

TABLE 2.—*Alpha-cellulose values by the volumetric and the gravimetric methods compared*

1	2	3	4	5	6
Materials	Gravimetric method for alpha cellulose	Volumetric method for alpha cellulose	Alpha-cellulose dichromate values	Total cellulose dichromate values	Bray and Andrews method for alpha cellulose
	Percent	*Percent*	*Milliliters*	*Milliliters*	*Percent*
1035 (no. 1 new white rag paper)	95.1	95.0	19.39	20.41	
	94.8	94.8	19.32	20.37	
	94.9	95.0	19.38	20.40	
		94.9	19.35	20.38	
Average	94.9	94.9	19.36	20.39	93.2
1009 (no. 1 old white rags) (washed)	90.6	90.6	20.46	22.58	
	90.4	90.4	20.40	22.58	
	90.6	90.1	20.38	22.61	
		90.5	20.45	22.60	
Average	90.5	90.4	20.42	22.59	90.4
1039 (refined sulfate pulp) (bleached sulfate)	84.0	83.9	18.42	21.94	
	84.0	84.2	18.51	21.97	
	83.6	84.2	18.48	21.95	
		84.2	18.49	21.97	
Average	83.9	84.1	18.48	21.96	83.8
1018 (soda pulp)	77.5	78.6	17.37	22.10	
	77.7	78.3	17.35	22.13	
	77.9	77.5	17.15	22.12	
		78.6	17.38	22.10	
Average	77.7	78.2	17.31	22.11	77.8
968 (refined sulfite pulp) ("Alpha" pulp)	90.8	90.5	20.09	22.19	
	90.6	90.6	20.08	22.16	
	90.7	90.5	20.05	22.15	
		90.6	20.04	22.13	
Average	90.7	90.6	20.06	22.16	89.8
1008 no. 1 new white rags (washed)	96.6	96.0	21.56	22.46	
	96.5	96.3	21.65	22.48	
	96.4	96.3	21.56	22.39	
		96.2	21.57	22.41	
Average	96.5	96.2	21.59	22.42	95.8

The gravimetric results are shown in column 2, table 2, and are to be compared with the volumetric results in column 3. The values agree well with those in the literature for the corresponding materials.[24] The values for alpha cellulose in column 6 are calculated according to the method of Bray and Andrews,[25] using, however, the theoretical factor 0.0124 g of cellulose per milliliter of 1.835N dichromate solution.

Aside from demonstrating the validity of the volumetric results, table 2 allows some interesting deductions concerning the behavior of the pentosans in these materials. Pulps 1039, 1018, and 988 had pentosan contents of 10.7, 21.3, and 3.8 percent, respectively.[26] It is evident that the distribution of pentosans between the alpha and the beta plus gamma fractions was such that the presence of pentosans did not cause serious differences between the volumetric and gravimetric results. This requires that the pentosans be distributed between the alkali-soluble and alkali-insoluble portions in approximately the same ratio as cellulose, which may be calculated from the following considerations. On the basis of the formula for pentosans, $C_5H_8O_4$, it is calculated that 1 ml of dichromate will oxidize 0.0220 g of pentosans, as against 0.0124 g of cellulose.

From the simple relation:

$$\frac{\frac{\text{wt of cellulose in alpha portion}}{0.0124}+\frac{\text{wt of pentosans in alpha portion}}{0.0220}}{\frac{\text{total wt of cellulose in sample}}{0.0124}+\frac{\text{total wt of pentosans in sample}}{0.0220}}=\frac{\text{volumetric alpha percent}}{100},$$

the following expression for the percentage of the total pentosans remaining with the alpha portion can be derived:

$x=(229/p)\ [(g-v)+v]$

x=percentage of total pentosans remaining with the alpha portion

p=total pentosans in sample, percent

g=gravimetric alpha-cellulose value (table 2, column 2)

v=volumetric alpha-cellulose value (table 2, column 3).

Substituting the corresponding data in this expression it is calculated that 79.8, 72.8, and 96.6 percent of the pentosans in the pulps 1039, 1018, and 988, respectively, remain in the alpha-cellulose portion. It is seen that these values for "alpha pentosans" are of the same order of magnitude as the values for alpha cellulose in the pulps. It may, of course, be argued that the difference between g and v is not significant, that perfect agreement between the gravimetric and volumetric results would be obtained if certain mechanical differences of treatment could be eliminated. In that case, $g-v=0$ and $x=v$, that is, the pentosans are distributed between the alpha and the beta plus gamma portions exactly as is the cellulose.

It was of interest to ascertain the precision of the method when unusually small samples are taken for analysis. Therefore, 0.03-g samples, corresponding to a piece of paper the size of an ordinary postage

[24] Lewis and Browning, Paper Trade J. 97, 39 (Dec. 1933). The method of Lewis and Browning gave the values 90.4% and 77.4% for pulps 988 and 1018, respectively.

[25] Bray and Andrews, Ind. Eng. Chem. 15, 377 (1923). See discussion also in Hawley and Wise, The Chemistry of Wood, p. 144-148 (Chemical Catalog Co., Inc., New York, N. Y.).

[26] See footnote (a) in table 1.

stamp, were taken of the materials 1035, 1039, and 1018. The process for separating the cellulose fractions was the same as above, except that a Schott fritted glass filtering crucible, no. 3, was used. The oxidimetric solutions used above were diluted tenfold for these experiments. The results obtained for the alpha-cellulose values for these 0.03-g samples were 94.2, 85.6, and 77.0 percent, respectively. It is seen that these values are in fair agreement with the corresponding ones listed in table 2. The writer believes that the precision when a 0.03-g sample is used could be increased by the use of a larger ratio of the volume of alkali to the weight of sample.

2. VOLUMETRIC RESULTS FOR BETA AND GAMMA CELLULOSE

The gravimetric determination of beta cellulose is usually extremely difficult and time consuming. Beta cellulose precipitates upon acidification of the filtrate from the alpha cellulose, as a very gelatinous substance. It clogs the pores of all filters, and usually requires from 2 to 4 hours for its separation. For that reason the directions [27] [28] advise coagulating the precipitate by boiling and filtering hot, followed by washing with hot water.

The boiling procedure, however, yields results which differ from those obtained when the separation is made at "room temperature", since the solubility of beta cellulose is rather strongly influenced by temperature. This is shown by experiments in which the gamma portions of acidified equal parts (1/10) of a beta+gamma filtrate from a 1-g sample of 1018 soda pulp were removed at various temperatures. After a mixture had been kept at a given temperature for several hours, with frequent stirring, the beta cellulose was allowed to settle at that temperature, and a definite part of the supernatant liquid was removed and analyzed volumetrically for dissolved cellulose. The results are listed in table 3. If a system in which the beta cellulose has been "coagulated" by heating to 100° C is allowed to cool, additional beta cellulose will precipitate.

Obviously, the beta cellulose should not be removed from the hot solution or washed with hot water if it is desired to obtain a measure of the cellulose, which simply precipitates upon acidification of the filtrate from the alpha cellulose. If the separation is made at room temperature, however, very little beta cellulose will be in the acidified solution. This can be seen simply by plotting temperature against beta cellulose content, using the data of table 3.

TABLE 3.—*Effect of temperature on the solubility of beta cellulose*

Temperature	Volume of dichromate for gamma portion	Apparent gamma cellulose	Beta cellulose
° C	*Milliliters*	*Percent*	*Percent*
20	0.31	3.4	18.4
60	.36	3.9	17.9
80	.43	4.7	17.1
100	.55	6.0	15.8

[27] Hawley and Wise, Chemistry of Wood, p. 145. Chemical Catalog Co., Inc., New York, N. Y. (1924.).
[28] Schwalbe-Sieber. Die Chemische Betriebskontrolle in d. Zellstoff-und Papier-Industrie, 3d ed., p. 411 Berlin (1931).

The extent to which the filtrate is acidified, implied in some methods as being of consequence, was found to have no appreciable effect upon the amount of beta cellulose precipitating, and, therefore, no appreciable effect upon the gamma-cellulose content over a very wide range (acidity$=10^{-6}$ N to $3N$). An amount of acid is, therefore, added which is known to be in excess of the base present, thereby avoiding the use of an indicator or of acetic acid, both of which were found to introduce large errors by reduction of dichromate. The values for the beta and gamma cellulose in the materials listed in table 2 are shown in table 4. The calculations were carried out as previously described.

TABLE 4.—*Volumetric results of the beta- and gamma-cellulose determinations*

Materials	Gamma cellulose dichromate values	Gamma cellulose	Beta cellulose
	Milliliters	*Percent*	*Percent*
1035 (rag paper)	0.26	1.3	3.8
	.27	1.3	3.9
	.25	1.2	3.8
	.26	1.3	3.8
Average		1.3	3.8
1009 (no. 1 old white rags)	0.30	1.3	8.1
	.33	1.5	8.1
	.32	1.4	8.5
	.39	1.7	7.8
Average		1.5	8.1
1039 (refined sulfate pulp)	2.50	11.4	4.7
	2.37	10.8	5.0
	2.42	11.0	4.3
	2.54	11.6	4.2
Average		11.2	4.7
1018 (soda pulp)	0.67	3.0	18.4
	.72	3.3	18.4
	.68	3.1	19.4
	.72	3.3	18.1
Average		3.2	18.6
988 (refined sulfite pulp)	0.98	4.4	5.1
	1.03	4.6	4.8
	1.03	4.6	4.9
	1.01	4.6	4.8
Average		4.6	4.9
1008 (no. 1 new white rags)	0.16	0.7	3.3
	.20	.9	2.8
	.22	1.0	2.7
	.22	1.0	2.8
Average		0.9	2.9

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REACTION OF WOOL WITH STRONG SOLUTIONS OF SULFURIC ACID

By Milton Harris, Ralph Mease, and Henry Rutherford [1]

ABSTRACT

Data on the effect on wool of treatment with solutions of sulfuric acid of different concentrations at 5, 25, and 50° C for 15 minutes and of an 80-percent solution of sulfuric acid at 25° C for different lengths of time are presented. The results suggest that strong sulfuric acid reacts with the basic groups in wool to form sulfamic acid derivatives. The acid-combining capacity of wool decreases and the base-combining capacity increases in proportion to the number of sulfamic acid groups formed.

CONTENTS

	Page
I. Introduction	343
II. Materials and methods	343
III. Results and discussion	345
1. Effect of temperature and acid concentration	345
2. Effect of the duration of treatment	346
3. Nature of the reaction of wool with strong sulfuric acid	346
4. Acidic and basic properties of the sulfamic acid derivative of wool	348
IV. References	350

I. INTRODUCTION

The use of strong solutions of sulfuric acid for the removal of cotton from mixtures with wool has been suggested by several investigators [1, 2, 3].[2] In studies relating to the analysis of wool-cotton textiles, Mease and Jessup [4] found that during treatment with an 80-percent solution of sulfuric acid,[3] wool gained from 5 to 8 percent in weight. Their results indicate that a relatively stable compound is formed, since this combined acid is not removed by prolonged washing with water or with solutions of ammonium hydroxide, sodium carbonate, or triethanolamine.

The present investigation was undertaken to study the nature of the reaction of wool with strong solutions of sulfuric acid and to study some of the properties of its product.

II. MATERIALS AND METHODS

The material used in this work was worsted cloth, plain weave, weighing 8 ounces per running yard (56 inches wide) or white worsted yarn prepared from raw wool which had been extracted with Stoddard

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[2] The numbers in brackets refer to literature references at the end of this paper.

[3] This concentration was obtained by mixing 80 ml of concentrated sulfuric acid (94 percent, sp gr 1.84) with 25 ml of water. The wool was immersed for 15 minutes in 80 to 100 times its weight of solution at room temperature.

solvent and washed with water. All the samples were further purified by extractions with alcohol and ether, followed by washing with water at about 50° C.

The samples of wool were treated with about 50 times their weight of sulfuric acid solutions. After the treatment with acid, the wool was immediately transferred to a large volume of running cold water and vigorously stirred in order to prevent local heating during the dilution of the excess of acid. The samples were then washed in running distilled water until the wash waters no longer gave tests for sulfate, the time required generally being about 72 hours.[4] The test for sulfate was made by allowing the samples of wool to remain in contact with a small amount of distilled water for about one-half hour and testing the liquor with barium chloride.

The percentage increase in weight of the wool before and after treatment was computed on the basis of the oven-dry weight.

The combined sulfuric acid in the wool was determined by the method of Mease [5]. Ammonia nitrogen was determined by measuring the ammonia liberated when the wool was boiled in a saturated solution of magnesium oxide.

The yellowing of the wool by the acid treatment was determined by measuring the reflectance of the sample with respect to a magnesium-oxide standard, at wave length 435.8 millimicrons, with a Martens photometer, mercury-arc lamp, and suitable filter. The reflectances of the dyed samples were determined with the same instrument at wave length 578 millimicrons, which is located in the region of maximum absorption for the blue dyes used.

The breaking strength of the cloth was determined on a pendulum-type testing machine using the strip method. The samples were 6 inches long and 1 inch wide, cut warpwise of the cloth. The distance between the jaws was 3 inches at the start of the test. All the samples were conditioned and tested in a room maintained at a relative humidity of 65 percent and a temperature of 70° F.

The acid- and base-combining capacities were determined by soaking samples of the wool for 4 hours (equilibrium appears to be reached in this time) in 0.1*N* solutions of hydrochloric acid,[5] sulfuric acid, and sodium hydroxide, the last being at 1 to 2° C to prevent decomposition of the wool fiber. The amount of acid or base combined was then found by titration of an aliquot of the mother liquor.

[4] Samples of wool which had been treated with a 4-percent solution of sulfuric acid for 30 minutes and then washed for 72 hours, regained 98 to 99 percent of their original acid-combining capacities.

[5] The limiting acid-combining capacity appears to be reached at about pH 1.

TABLE 1.—*Effect on wool of treatment with different concentrations of sulfuric acid at 5, 25, and 50° C for 15 minutes*

Concentration of H_2SO_4 by weight	SO_4 from sulfuric acid treated wool	Reflectance [1] R_s/R_{MgO}	Breaking strength of 1-in. strip	Ammonia nitrogen
TEMPERATURE 5° C				
Percent	*Percent*	R_s/R_{MgO}	lb	mg/g
19	0.42	46.2	29	0.43
34	.66	47.1	29	.42
48	.68	47.0	29	.41
60	.64	47.5	29	.48
69	.69	46.2	29	.43
80	1.02	46.3	27	.43
85	3.42	44.3	28	.50
94	11.00	43.9	26	1.67
TEMPERATURE 25° C				
19	0.88	45.6	28	0.52
34	1.20	47.8	28	.48
48	1.21	46.1	28	.68
60	1.38	46.0	26	.64
69	1.37	45.3	27	.52
80	6.91	43.2	26	.60
85	10.20	40.4	24	1.20
94	11.70	39.1	23	2.28
TEMPERATURE 50° C				
19	0.65	47.6	28	0.43
34	.71	47.1	26	.63
48	.72	47.0	25	.62
60	3.50	41.2	18	.70
69	3.79	37.0	16	.79
80	6.14	35.4	19	.92
85	8.13	34.7	21	.91
94	9.39	35.2	21	1.60

[1] The values represent the ratio of the brightness of the sample to that of a standard white magnesium-oxide surface under the same conditions of illumination and observation, for light of wave length 435.8 millimicrons. The darker (or yellower as in this case) the specimen, the smaller the value for light reflected.

III. RESULTS AND DISCUSSION

1. EFFECT OF TEMPERATURE AND ACID CONCENTRATION

In view of the procedures [4] recommended for the removal of cotton from mixtures with wool by the sulfuric acid method, it seemed advisable to study first the effect of different concentrations of sulfuric acid on wool. The effects of the different treatments at 5, 25, and 50° C for 15 minutes are summarized in table 1. The results indicate marked changes in the amount of acid combined between 69- and 80-percent sulfuric acid at 5 and 25° C and between 48- and 60-percent acid at 50° C. Since wool, in an 80-percent solution of sulfuric acid at 25° C, reacts with a relatively large amount of acid, as shown by the sulfate analyses, and since the reaction is accompanied by comparatively little deterioration of the fiber, as evidenced by reflectance, breaking strength and ammonia-nitrogen determinations, this concentration and temperature of acid solution were chosen for the further studies.

2. EFFECT OF THE DURATION OF TREATMENT

Samples of wool were treated with an 80-percent solution of sulfuric acid at 25° C for different lengths of time, and washed as previously described. The increase in weight and the sulfate obtained from the treated wool are recorded in table 2. The data indicate that a maximum increase in weight is obtained in the treatment for 30 minutes. On treatment for periods longer than 30 minutes, the wool not only decreased in weight, but the amount of sulfate obtained from it also decreased. The appearance of the wool treated for periods of longer than 30 minutes indicated that considerable degradation had occurred.

TABLE 2.—*Effect on wool of treatment with an 80-percent solution of sulfuric acid at 25° C for different lengths of time*

Duration of treatment	Increase in weight	SO_4 from treated wool
Minute	*Percent*	*Percent*
3	0.56	0.81
6	2.35	3.53
9	3.82	4.82
12	5.60	6.37
15	6.20	7.23
20	6.77	7.90
30	7.19	8.38
40	7.03	8.34
60	6.71	7.78
105	6.58	7.17
150	4.93	6.74

3. NATURE OF THE REACTION OF WOOL WITH STRONG SULFURIC ACID

Of the two principal theories to account for the acid taken up by wool, namely, the chemical and the physical or adsorption theories, the work of Knecht [6], Mayer [7], Porai-Koschitz [8], and Speakman [9] favors the former. These investigators showed that wool has an acid-combining capacity of about 0.80 millimole of acid per gram of wool. In addition, Harris and Kanagy [10] showed that this combined acid may be accounted for by the free amino groups and by the guanidine nucleus of the arginine in wool. Speakman [9], utilizing his own data and also the data of Dietl [11], Fort and Lloyd [12], and Georgievics and Pollack [13] to calculate the amounts of acid combined as a function of pH, demonstrated that sulfuric acid was practically monobasic in reaction with wool.

On the basis of the above work, the following equations which give a schematic representation of two possible mechanisms by which sulfuric acid may be taken up and held by the basic groups in wool, are postulated.

$$(1)\ RNH_2+H_2SO_4 \rightleftarrows RNH_3.HSO_4$$
$$(2)\ RNH_2+H_2SO_4 \rightarrow RNHSO_3H+H_2O,$$

where R represents the portion of the wool molecule to which the basic group is attached.

The acid in the compound formed in equation 1 should be reversibly held; that is, it should be slowly removed by washing with water, rapidly removed by pyridine [14], triethanolamine [15], sodium terephthalate [15] and other alkaline reagents, and readily replaceable by

acid dyestuffs. Equation 1 indicates the reaction which is assumed to take place in dilute solutions of sulfuric acid.

On the other hand, the acid in the compound formed according to equation 2 should be irreversibly held under the conditions mentioned above. It appears that such a compound would be formed only under dehydrating conditions, for example, in the presence of strong sulfuric acid, and that the acid would be removed by hydrolytic processes [6] according to the reverse of equation 2. In other words, the fact that sulfate is obtained when the acid-treated wool is analyzed by the method of Mease [5], is no indication that it existed as such in the wool.

It should be possible, therefore, to determine which type of compound is formed when wool is treated with strong or dilute solutions of sulfuric acid by recalculating the data on the SO_4 obtained from the

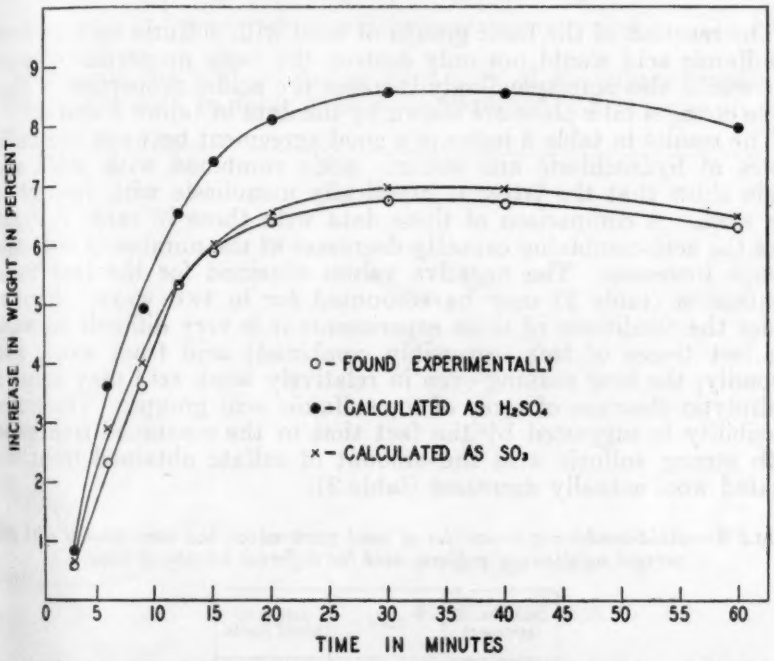
INCREASE IN WEIGHT IN PERCENT
TIME IN MINUTES
0 5 10 15 20 25 30 35 40 45 50 55 60
1 2 3 4 5 6 7 8 9
○ – FOUND EXPERIMENTALLY
● – CALCULATED AS H₂SO₄
× – CALCULATED AS SO₃

FIGURE 1.—*Comparison of the actual increase in weight of wool resulting from treatments with an 80-percent solution of sulfuric acid at 25° C for different lengths of time with the increase obtained by calculating the* SO_4 *obtained from the treated wool as* H_2SO_4 *and as* SO_3.

treated wool in terms of H_2SO_4 and SO_3, and comparing the calculated weights with the actual increase in weight of the wool after treatment with sulfuric acid. The data obtained by recalculating the data given in table 2 are shown graphically in figure 1. The results suggest that the reaction of wool with the strong solutions of sulfuric acid has proceeded according to equation 2, and that a sulfamic acid derivative of wool has been formed.

That the reaction of wool with dilute solutions of sulfuric acid proceeds in a different manner is demonstrated by the following

[6] The hydrolytic conditions necessary for the reverse of equation 2 are so drastic as to cause degradation of the wool fiber. Accordingly, equation 2, which represents the manner in which the acid is assumed to be held by the original wool fiber, is written as an irreversible reaction.

experiment. A 2-g sample of wool was treated with 100 ml of a 4-percent solution of sulfuric acid for 30 minutes, after which the excess of acid was squeezed out by hand. The sample was then soaked for 15 seconds in 100 ml of distilled water, squeezed again, and then partially dried by allowing it to remain in contact with air at room temperature for about 6 hours. It was finally dried to constant weight in the oven at 105° C. The sample showed a 5.5 percent increase in weight. The calculated increases in weight, based on the sulfate analyses, were 5.3 percent calculated as H_2SO_4 and 4.3 percent calculated as SO_3. These results suggest that this reaction has proceeded as shown in equation 1.

4. ACIDIC AND BASIC PROPERTIES OF THE SULFAMIC ACID DERIVATIVE OF WOOL

The reaction of the basic groups of wool with sulfuric acid to form a sulfamic acid would not only destroy the basic properties of wool but would also correspondingly increase the acidic properties. That these changes take place are shown by the data in tables 3 and 4.

The results in table 3 indicate a good agreement between the millimoles of hydrochloric and sulfuric acids combined with wool and again show that the latter is practically monobasic with respect to the wool. A comparison of these data with those in table 2 shows that the acid-combining capacity decreases as the number of sulfamic groups increases. The negative values obtained for the last three treatments (table 3) may be accounted for in two ways. Firstly, under the conditions of these experiments it is very difficult to wash the last traces of free (reversibly combined) acid from wool, and secondly, the long soaking even in relatively weak acid may cause a hydrolytic cleavage of some of the sulfamic acid groups. The latter possibility is suggested by the fact that in the continued treatment with strong sulfuric acid the amount of sulfate obtained from the treated wool actually decreases (table 2).

TABLE 3.—*Acid-combining capacities of wool yarn which has been treated with 80-percent solutions of sulfuric acid for different lengths of time*

Duration of treatment	HCl	Acid-combined H_2SO_4
Minutes	*Millimole*	*Millimole*
0	0.81	0.84
3	.62	.63
6	.34	.35
9	.28	.33
12	.21	.26
15	.00	.04
20	−.08	−.09
30	−.08	−.06
40	−.11	−.09

TABLE 4.—*Alkali-combining capacities of wool yarn which has been treated with 80-percent solutions of sulfuric acid for different lengths of time*

Duration of treatment	NaOH combined	Increase in base-combining capacity of the treated wool	
		Found	Calculated on the basis of the combined SO_3
Minutes	*Millimoles*	*Millimole*	*Millimole*
0	0.64		
3	.80	0.16	0.09
6	1.17	.53	.38
9	1.29	.65	.52
12	1.39	.75	.70
20	1.50	.86	.88
40	1.62	.98	.94

Although the acid-combining capacities of the treated wools decrease, the data in table 4 show a corresponding increase in base-

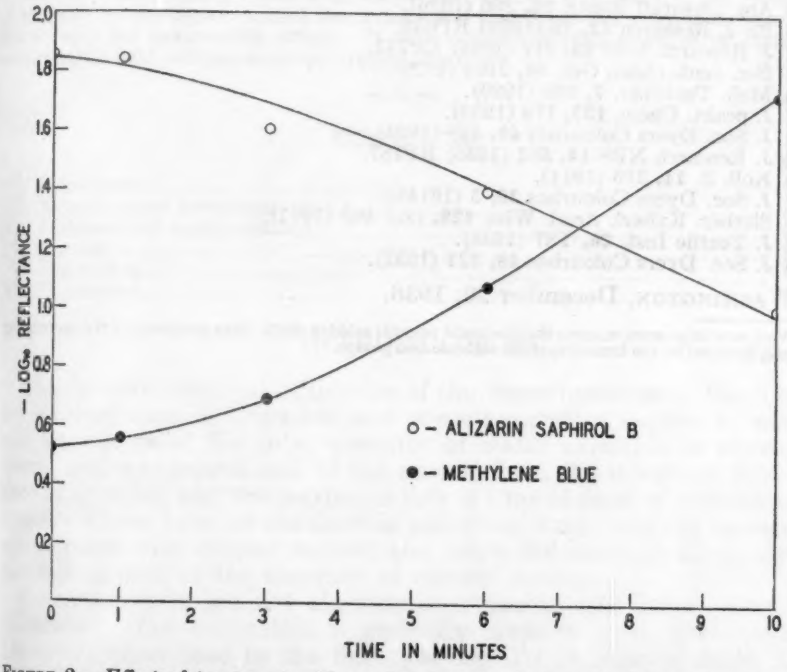

FIGURE 2.—*Effect of treatment with an 80-percent solution of sulfuric acid on the dyeing characteristics of wool cloth, as shown by change in reflectance of light at wave length 578 millimicrons.*

combining capacity with an increasing number of sulfamic acid groups. The increase in alkali-combining capacity, as found experimentally, is in good agreement with the values which were calculated on the assumption that 1 mole of the combined SO_3 reacts with 1 mole of sodium hydroxide. This also constitutes further evidence that the product of the reaction of wool with strong sulfuric acid is a sulfamic acid derivative since, if the acid were held as shown in equation 1, 2 moles of sod-

ium hydroxide would be required for each mole of combined acid [14], because the wool is regenerated.

The changes in acidic and basic properties of the treated wool are also manifested in the dyeing characteristics of the fiber. Samples of wool cloth which had been treated with 80-percent solutions of sulfuric acid for different lengths of time were dyed in the same bath containing approximately 2 percent of alizarin saphirol *B* (based on the weight of fiber). A second set of the acid-treated samples were similarly dyed using methylene blue.

The curves in figure 2 show that the amount of acid dyestuff (alizarin saphirol *B*) absorbed decreases and the amount of basic dyestuff (methylene blue) absorbed increases with increasing time of treatment with strong sulfuric acid.[7]

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[14] J. Textile Inst. **26,** T87 (1935).
[15] J. Soc. Dyers Colourists **48,** 321 (1932).

WASHINGTON, December 29, 1936.

[7] Work now in progress suggests that the resist towards acid dye stuffs, often produced in the carbonizing process, is caused by the formation of the sulfamic acid groups.

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PERFORMANCE CHARACTERISTICS OF A WATER CURRENT METER IN WATER AND IN AIR

By Galen B. Schubauer and Martin A. Mason

ABSTRACT

The effect of density on the performance of a water current meter of the cup-wheel type, known as the small Price meter, was investigated by calibrating the meter first in water by towing it in a rating tank, and second in air by placing the meter in a wind tunnel. The change from water to air produced a change in density by a factor of approximately 800. It was found that the revolutions of the cup wheel during 1 foot of travel of the fluid was a function of the product of velocity by the square root of the density and that Reynolds number and turbulence have no measurable effect. It was concluded that changes of density occurring in field use can cause no appreciable error.

CONTENTS

		Page
I.	Introduction	351
II.	Experimental investigation	352
III.	Dimensional considerations	353
IV.	Results	354
V.	Discussion	357
VI.	Conclusion	360

I. INTRODUCTION

The development and utilization of the water resources of the country for flood control, irrigation, and power generation require an accurate knowledge of the total quantity of water available in streams, rivers, and watersheds and of the normal flow, the minimum flow in time of drought, and the maximum flow in time of flood of streams and rivers. These data are obtained in part from water velocity measurements made with current meters, and hence the accuracy of the data depends in part on the accuracy of current meters.

Current meters are not absolute instruments and hence must be calibrated. The calibration is generally made in clear, fresh water. However, when used in the field, particularly in time of flood, the water is by no means clear, carrying silt, mud, and debris. Likewise, meters are occasionally used for measurements in salt water. The question immediately arises as to the effect of these departures from the conditions of the calibration on the indications of the meter.

It is known that the mixtures or solutions encountered in the field are more dense than clear, fresh water; but whether or not the effect on the meter is the same as that which would be produced by a homogeneous fluid of the same density cannot be answered simply. Certainly, one effect of silt and mud is to increase the inertia of the

fluid and to this extent the effect on the indications of the meter will be similar to that of a fluid of greater density. If the water carries particles of considerable magnitude, such as pebbles, or if the mixture is so thick as to be much more viscous than water, other effects are obviously present. Calibrations of a current meter in homogeneous fluids of different density may be expected to give some indication of the behavior of the meter in mixtures or solutions of densities not differing greatly from that of clear, fresh water.

In order to determine the effect of the density on their calibration, two current meters were rated in homogeneous media of different density: (1) in water in the rating tank of the National Bureau of Standards, and (2) in air in the Bureau's 4½-ft wind tunnel. By this means a density change by a factor of about 800 was secured.

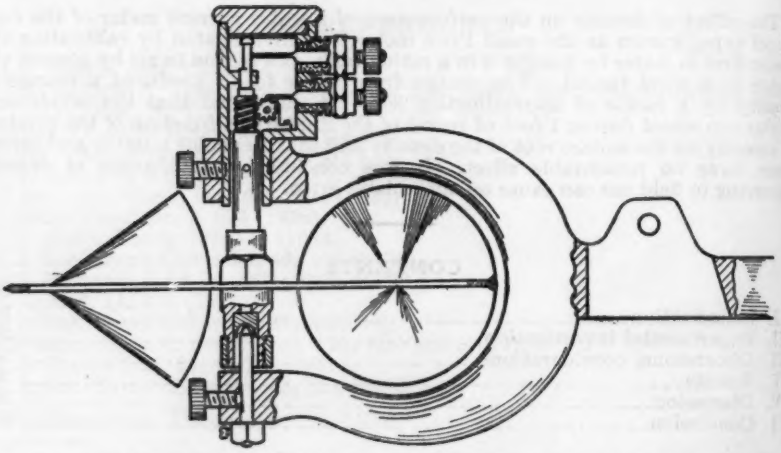

FIGURE 2.—*Diagram of small Price water current meter, showing the arrangement of bearings and contact mechanism.*

A comparison of the rates of rotation of the meters at the same relative speed of the fluid with respect to the meter was intended to show the effect, if any, of density variation. Since, however, the change from the rating tank to the wind tunnel involved differences in turbulence and Reynolds number, as well as density, the possible effect of these additional variables had to be considered.

The only other work known in which an attempt was made to compare the performance of a water current meter in both water and air is that reported for a propeller type meter in 1901 by Hajós.[1] Unfortunately, the information given about the tests is too meager to permit an analysis of the results for comparison with the results presented here.

II. EXPERIMENTAL INVESTIGATION

The meters used in the study are known as small Price meters (figs. 1 and 2) and are of the cup-wheel type, the wheel revolving about a vertical axis. They depend for their operation on the differential pressure acting on the open and closed ends of the cups. Figure

[1] S. Hajós. Beiträge zur Frage über die Umlaufswerte Woltmann'scher Flügel. Deutsch-Oesterreich Ungarischer Verband für Binnenschifffahrt, new series no. IX (1901).

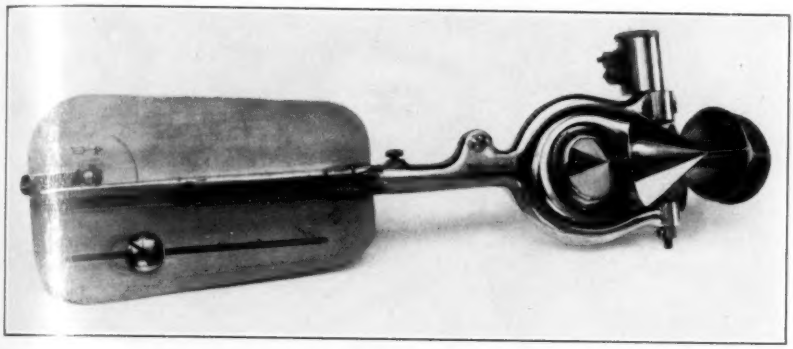

FIGURE 1.—*Small Price water current meter.*

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2 shows the constructional details of this type of meter. The calibration of the meter consists in the determination of the relation between the rate of rotation of the cup-wheel and the velocity of the fluid relative to the meter, for the range of velocities expected to be encountered in the field. In the rating tank, the calibration is made by towing the meter through still water; in the wind tunnel, the calibration is made by drawing air past the stationary meter.

The experimental procedure was arranged as follows. The two meters were first rated in water, then in air, and again in water to determine whether changes in the meter had occurred during the high-speed running in air. The meters were mounted singly below the towing car 24 inches below the surface of the water on a rod suspension. The same suspension equipment was used in the wind tunnel, the upper end of the rod being attached to the top of the wind tunnel 27 inches above the meter. Complete tests were made of two meters to avoid possible errors resulting from irregularities in any one instrument.

III. DIMENSIONAL CONSIDERATIONS

The characteristics of current meters of either the propeller or the cup-wheel type are usually expressed in terms of the "apparent pitch", defined as the actual distance, in feet, traveled by the fluid while the propeller or cup wheel makes one turn. The reciprocal of this quantity, termed "reciprocal of apparent pitch" or simply "revolutions per foot", is more commonly used in connection with the cup-wheel type, for purposes of precise calibration, and for this reason will be used here. If D is the diameter of the cup wheel, in feet, it follows that revolutions per foot $\times \pi D$ is a dimensionless ratio expressing the ratio of the peripheral distance traveled by the cups during rotation for a given period of time to the distance traveled by the fluid in the same time.

If, from the several quantities which may affect the rate of rotation of the cup wheel, we choose only those of importance in the present treatment, we then have:

U, velocity of the fluid
ρ, density of the fluid
μ, viscosity of the fluid
$\sqrt{\overline{u^2}}$, turbulence expressed in terms of the root-mean-square value of the turbulence velocity fluctuations
D, some dimension of the instrument, such as the diameter of the cup wheel
T, opposing torque arising from bearing and contact friction when no load is imposed by the drag of the cup wheel
ΔT, change in opposing torque resulting from change in bearing friction attributable to the drag of the cup wheel

It is found by dimensional considerations that revolutions per foot $\times \pi D$ may be expressed in terms of dimensionless ratios of the foregoing quantities by the following functional relation:

$$\text{Revolutions per foot} \times \pi D = F\left(\frac{T+\Delta T}{\rho U^2 D^3}, \frac{UD\rho}{\mu}, \frac{\sqrt{\overline{u^2}}}{U}\right), \qquad (1)$$

where F is an unknown function, the nature of which may be determined by experiment. The quantity $UD\,\rho/\mu$ is the Reynolds number, and $\sqrt{\overline{u^2}}/U$ is the intensity of the turbulence.

Since the drag load on the bearings is proportional to ρU^2D^2, the change in frictional torque ΔT may be assumed to be proportional to ρU^2D^3. If this assumption is correct $\Delta T/\rho U^2D^3$=constant.

The assumption is correct provided the geometrical form of the bearings and the coefficient of friction do not depend on the magnitude of the drag. We may, therefore, replace the first member on the right of relation 1 by $\frac{T}{\rho U^2D^3}+A$, where A is simply a constant. We may then rewrite the functional relation more simply as

$$\text{Revolutions per foot}=\frac{1}{\pi D}F_1\left(\frac{T}{\rho U^2D^3}+A,\frac{UD\rho}{\mu},\frac{\sqrt{\overline{u^2}}}{U}\right), \qquad (2)$$

where F_1 is a new function.

Dimensional considerations show only the combinations of variables upon which the quantity, revolutions per foot, depends. The relative importance of the three members on the right-hand side of relation 2 and the nature of the function can best be found by experiment.

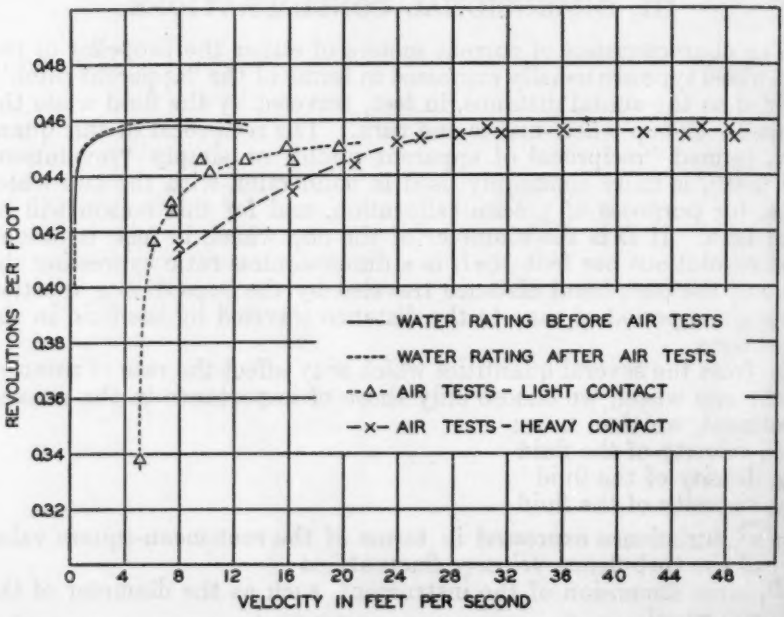

FIGURE 3.—*Relation between revolutions per foot and velocity of water and air.*
Meter WR-1495.

IV. RESULTS

The results are given in figures 3 to 8, inclusive. The figures are given in pairs showing similar diagrams for each meter, the pairs consisting of 3 and 4; 5 and 6; 7 and 8. Figures 3 and 4 each show two sets of curves giving the relation between revolutions per foot and water velocity in one case and air velocity in the other. The curves for the two media differ greatly, especially at the lower velocities. In order to account for the difference between the curves, it is necessary to consider the relative effects of the three members on the right of relation 2,

$$\frac{T}{\rho U^2 D^3} + A, \frac{UD\rho}{\mu}, \frac{\sqrt{\overline{u^2}}}{U}$$

the first two of which differ in the two media because of the change in ρ and μ, and the third because of the change in flow conditions. It is assumed that T, which depends on the condition of the bearings and the tension of the contact brush, remains the same in the two media. For a particular value of the velocity the change from water to air raised $T/\rho U^2 D^3$ by a factor of approximately 800 and lowered $UD\rho/\mu$ by a factor of about 13. The amount of turbulence in the water of the rating tank was unknown, although it was probably smaller than

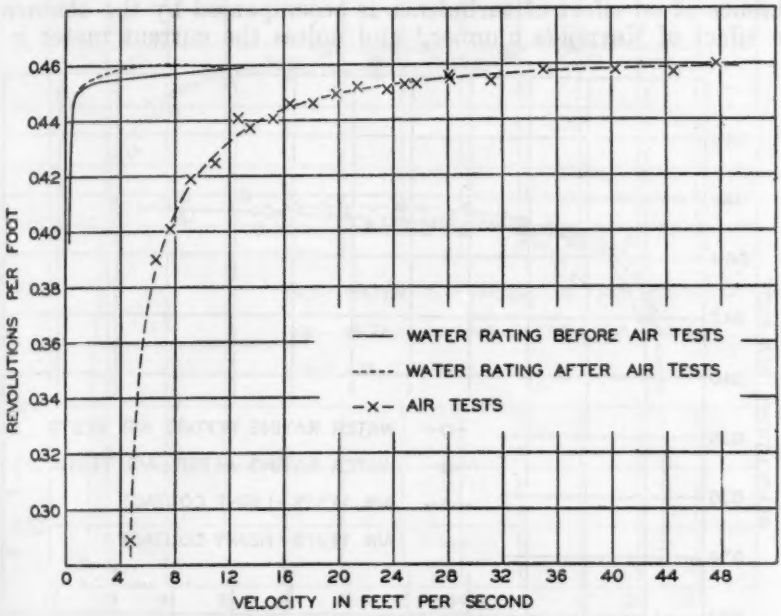

FIGURE 4.—*Relation between revolutions per foot and velocity of water and air.* Meter WR-1496.

that in the wind tunnel, since the water in the rating tank was allowed to become sensibly still between each observation run.

The intensity of turbulence in the wind tunnel under ordinary conditions was 0.85 percent ($100\sqrt{\overline{u^2}}/U=0.85$). Fortunately, it was possible in the wind tunnel to vary $\sqrt{\overline{u^2}}/U$ independently of $T/\rho U^2 D^3$ and $UD\rho/\mu$. This was accomplished by placing completely across the upstream section of the tunnel a square-mesh screen made of round wooden rods ⅝ inch in diameter, spaced 3¼ inches apart.[2] At the current-meter location, which was 7.6 feet downstream from the screen, the intensity of the turbulence was 2.7 percent. After a thorough investigation of the velocity distribution at the current-meter loca-

[2] For a more detailed account of this method of producing turbulence and the nature of the turbulence itself see: Measurements of Intensity and Scale of Wind-Tunnel Turbulence and their Relation to the Critical Reynolds Number of Spheres. Nti. Advisory Comm. Aero. Tech Rept. 581 (1937).

tion, both meters were run at this higher turbulence. By comparing runs made at the higher turbulence with those given in figures 3 and 4, which correspond to the lower turbulence, it was found for both meters that the rates were the same for 2.7-percent turbulence as for 0.85 percent; or if any differences did exist, they were too small to be detected above the experimental scatter. In contrast to this result, the rate of a Robinson cup anemometer of the old standard type with four smooth hemispherical cups was found to be increased by 5 percent at the higher turbulence. It was concluded, therefore, that the term $\sqrt{\overline{u^2}}/U$ could be dropped from relation 2 as being without effect on the rating of cup-wheel current meters of the small Price type.

It has been found generally in aerodynamic investigations that an absence of an effect of turbulence is accompanied by the absence of an effect of Reynolds number,[3] and unless the current meter is an

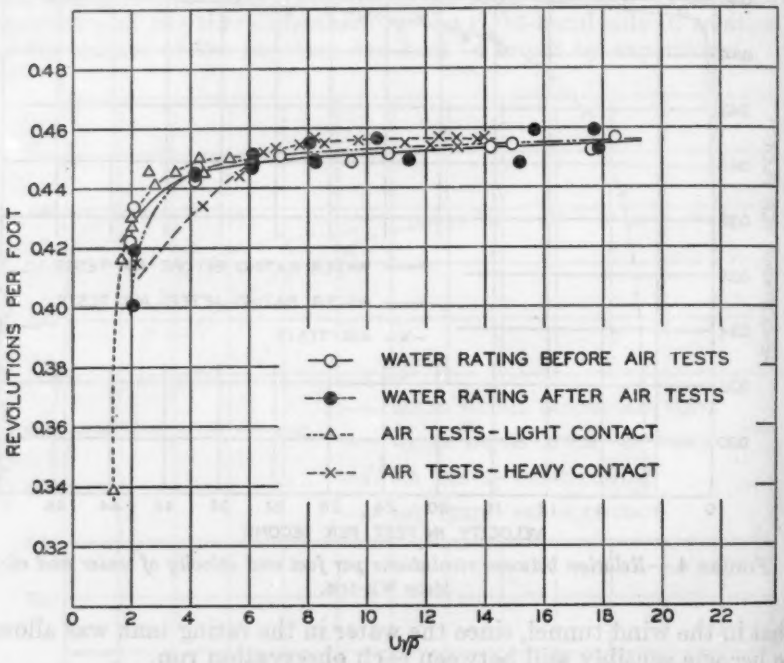

FIGURE 5.—*Relation between revolutions per foot and* $U\sqrt{\rho}$.
U=velocity of water or air in feet per second.
ρ=Density of water or air, in pounds per cubic foot.
Meter WR-1495.

exception, the same result which permits the dropping of $\sqrt{\overline{u^2}}/U$ suggests also the omission of $UD\rho/\mu$ in relation 2. The tests with two different amounts of turbulence lead, therefore, to the supposition that relation 2 might be simplified to

$$\text{Revolutions per foot}=\frac{1}{\pi D}F_2\left(\frac{T}{\rho U^2 D^3}+A\right), \tag{3}$$

or with T and D constant and ρU^2 as the only variable quantity

$$\text{Revolutions per foot}=F_3(U\sqrt{\rho}), \tag{4}$$

[3] Hugh L. Dryden, *Turbulence companion of Reynolds number*. J. Aero. Sci. 1, no. 2, 67 (April 1934).

where the new function F_3 has absorbed the constants and taken care of the inversion.

The foregoing reasoning simply provides justification for testing relation 4; that is, that revolutions per foot is a function of $U\sqrt{\rho}$ only. The test is applied in figures 5 and 6, where the results of figures 3 and 4 have been replotted with revolutions per foot as ordinates against $U\sqrt{\rho}$ as abscissas. It is seen that the curves for water and air have been brought into close agreement, approximating the condition of a single curve, as indicated by relation 4. In figure 5 (also in fig. 3) the two curves for air show the marked effect of changing

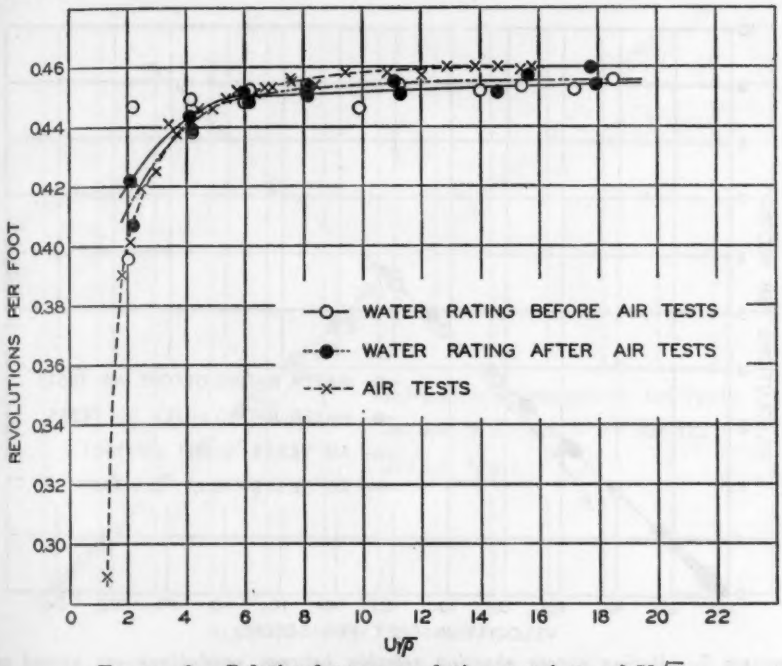

FIGURE 6.—*Relation between revolutions per foot and* $U\sqrt{\rho}$.
U=velocity of water or air in feet per second.
ρ=Density of water or air in pounds per cubic foot.
Meter WR-1496.

the tension of the contact brush and thereby changing T. In view of this sensitivity to small changes in friction and the drastic nature of the changes from water to air, it is not surprising that the over-all agreement is not closer than 1 percent. In fact, the approximation to a single curve must be regarded as remarkably good, a condition which amply supports the validity of relation 4 or the more general relation 3.

V. DISCUSSION

There is, therefore, an effect of density, the magnitude of which increases with T. As T approaches zero, $T/\rho U^2D^3$ approaches zero, and the revolutions per foot will show less and less dependence on both ρ and U; that is, curves similar to those of figures 3, 4, 5, and 6 will show less and less tendency to drop at low values of U or $U\sqrt{\rho}$.

If instead of decreasing $T/\rho U^2D^3$ by decreasing T, we do so by increasing ρ, the effect is the same. Of the latter we have examples in figures 3 and 4, where it may be seen that the flat, horizontal part of the curves persists to lower velocities for the case where the density is the higher. Further increases in density would simply push the knee of the curve to still smaller velocities. It is obvious at once that a density greater than that of water can have very little effect on the performance of the meters, except at very low velocities. For example, it may be seen by the aid of either figures 5 or 6 that if either of these meters were run in a fluid twice as dense as water flowing with a velocity of 0.5 feet per second, the rates would be only about

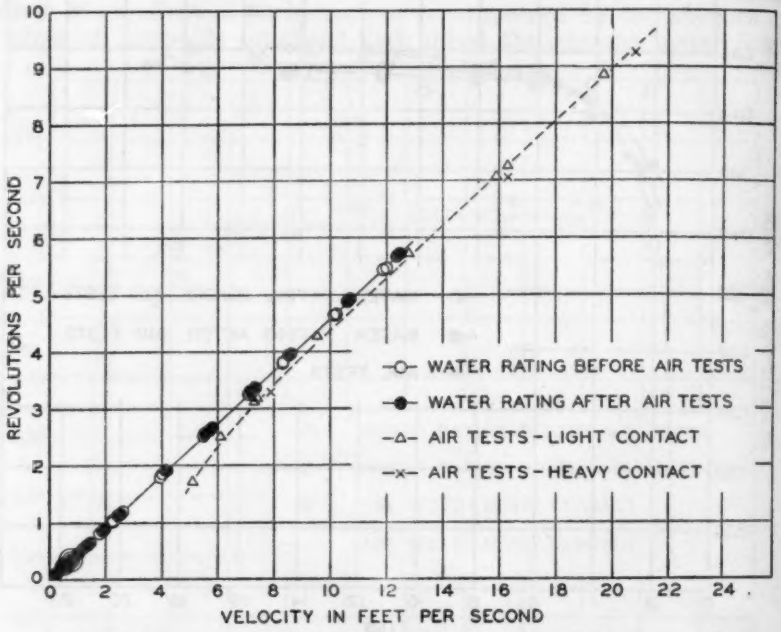

FIGURE 7.—*Rating curves showing relation between revolutions per second and velocity of water and air.*

Meter WR-1495.

2 percent higher than they would be in water. At higher velocities the difference would be still less.

Lowering the density will, in general, have a greater effect than increasing the density, but as long as the density is near that of water the effect will not be large. As a second example, suppose the density of the fluid to be half that of water. Again, using figures 5 or 6, we find that the rate of a meter in such a fluid flowing with a velocity of 0.5 feet per second would be lowered by 3 percent below that for water. Since halving the density has the same effect as doubling the frictional torque, we may apply the example to a meter which for some reason has had its bearing friction doubled. Under the conditions of higher friction the rate of this meter would be lowered by 3 percent when running in water flowing at 0.5 feet per second. At higher velocities the change would be less.

This condition is further illustrated by figures 7 and 8, which show the usual type of rating curve. In these figures the curves giving the water rating do not depart perceptibly from a straight line, but actually if plotted to a more open scale the lines could be seen to curve toward the velocity axis at the low velocities, in the manner of the curves giving the air rating, and to intercept the abscissa at the starting velocity. A fluid with a greater density than that of water would yield a curve with a straight portion extending to still smaller velocities and having a smaller intercept on the velocity axis. Since the line is already quite straight it is apparent that further increase of density can have little effect. However, decreasing the density or

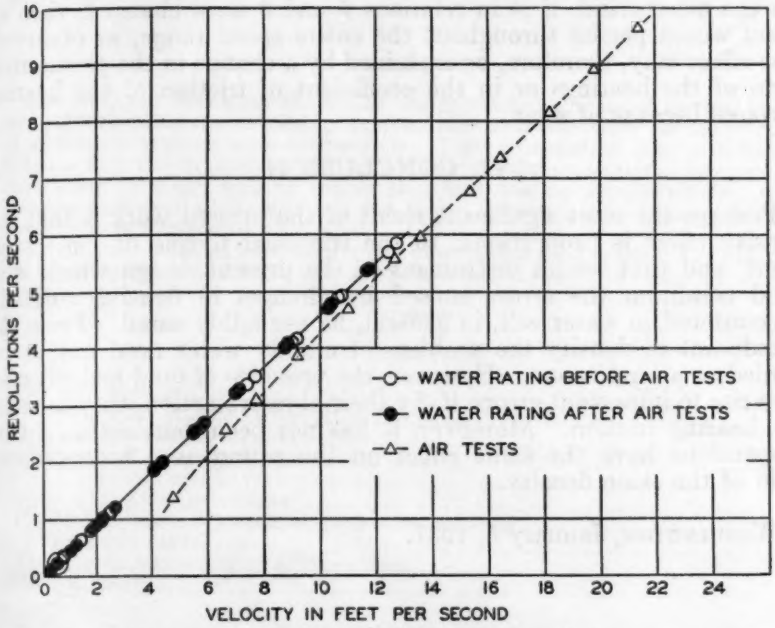

FIGURE 8.—*Rating curves showing relation between revolutions per second and velocity of water and air.*

Meter WR-1496.

increasing the friction can have an effect of any magnitude since the line can be given any amount of curvature.

If it is desired to obtain a rating curve, such as shown in either figures 7 or 8, for some density other than that for which the meter was calibrated, the following procedure may be adopted. From calibration data consisting in rates of rotation of the cup wheel corresponding to known velocities and the known density of the fluid, a curve like those shown in either figures 5 or 6 is computed. Corresponding to any value of the ordinate a new velocity U_1 is computed by

$$U_1\sqrt{\rho_1}=U_c\sqrt{\rho_c},$$

where U_c and ρ_c are the velocity and density pertaining to calibration and U_1 is the velocity at the density ρ_1 which will yield the same value

of the ordinate, i. e., the same value of revolutions per foot. Having U_1, the new rate of rotation corresponding to it is revolutions per second $= U_1 \times$ revolutions per foot.

In this way a new set of rates and velocities corresponding to the density ρ_1 may be calculated and the new rating curve obtained.

An examination of figures 3 and 4 will reveal the fact that both meters ran faster throughout the velocity range during the second test in water following the tests in air. This phenomenon has been observed generally when meters have been recalibrated after much use. The effect is usually attributed to "running in", a condition of wear which favors faster running. If T were decreased due to wear, the increased rate would be noticeable only at the lower velocities. On the other hand, if A in relations 2 and 3 were changed, then an effect would persist throughout the entire speed range, as observed. The effect may, therefore, be explained by a change in the geometrical form of the bearings or in the coefficient of friction of the bearing surfaces because of wear.

VI. CONCLUSION

Perhaps the most significant result of the present work is that the density effect is proportional to the frictional torque of the instrument; and that for an instrument of the present design which is in good condition the errors caused by changes in density normally encountered in water will, in general, be negligibly small. From the standpoint of density the problem of muddy water need not be regarded as a serious one. However, the presence of mud and silt may give rise to important errors, if, by their abrasive action, they increase the bearing friction. Moreover, it has not been demonstrated that suspensions have the same effect on the rating as a homogeneous fluid of the same density.

WASHINGTON, January 5, 1937.

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RESEARCH PAPER RP982

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SOIL-CORROSION STUDIES, 1934. FIELD TESTS OF NONBITUMINOUS COATINGS FOR UNDERGROUND USE

By Kirk H. Logan and Scott P. Ewing

ABSTRACT

The National Bureau of Standards has conducted a series of tests of metallic and other nonbituminous coatings to determine their suitability for the protection of structures exposed to corrosive soils. Tests of calorized pipe in a few soils indicate that this type of coating affords only partial protection. Lead corrodes sufficiently in many soils to render thin lead coating unsatisfactory. Of the metallic coatings tested, zinc was the best. However, zinc coatings gradually deteriorate in many soils.

Several new coatings have been under observation for 2 years. For this period of exposure, the best of these were a vitreous enamel and two rather thick rubber compounds.

CONTENTS

	Page
I. Introduction	361
II. Properties of soils at test sites	362
III. Metallic coatings	367
1. Lead-coated pipe	367
2. Aluminum (calorized)	370
3. Zinc (galvanized)	371
IV. Mill and foundry scale as protective coatings	380
V. Parkway cable	381
VI. Miscellaneous nonmetallic coatings	382
VII. Summary	387

I. INTRODUCTION

In 1922 the National Bureau of Standards began its study of metallic coatings for underground use by the burial of specimens of galvanized pipe. Two years later, studies of the effects of the weight or thickness of the coating and of the type of base material to which the coating was applied were undertaken. Some other metallic coatings have also been investigated. In 1932 there were included in the investigation of corrosion-resistant materials several types of recently developed coatings. This report gives the results of the tests of all of the above-mentioned coatings. With a few exceptions, the coatings have been applied to sections of steel pipe. The descriptions of the coatings buried prior to 1932 are given in Technologic Paper 368,[1] which gives also descriptions of the soils in which the tests were conducted.

[1] K. H. Logan, S. P. Ewing, and C. D. Yeomans, *Bureau of Standards soil-corrosion studies: I. Soils, materials, and results of early observations.* Tech. Pap. BS **22**, 447 (1928) T368, 50¢.

II. PROPERTIES OF SOILS AT TEST SITES

Table 1 gives the names and locations of the soils to which the specimens were exposed. Some of the physical and chemical properties of these soils are given in table 2. The drainage was estimated by an examination of the soil and topography at the test site. The moisture equivalent is the percentage of moisture the soil will retain against a centrifugal force of 1,000 gravity. It is a measure of the moisture content of a soil which after saturation has reached equilibrium with gravitational and capillary forces. The methods used to determine the moisture equivalent, pH, and the chemical composition of the soil extract, are given in Research Paper 918.[2] Methods for measuring total acidity are given in Research Paper 539.[3]

TABLE 1.—*Identification of soils*

Soil	Soil type	Location	Cooperating organization
1	Allis silt loam	Cleveland, Ohio	East Ohio Gas Co.
2	Bell clay	Dallas, Tex	Dallas Gas Co.
3	Cecil clay loam	Atlanta, Ga	Department of Public Works.
4	Chester loam	Jenkintown, Pa	Philadelphia Electric Co.
5	Dublin clay adobe	Oakland, Calif	East Bay Municipal Utility District.
6	Everett gravelly, sandy loam.	Seattle, Wash	Department of Public Works.
7	Silt loam	Cincinnati, Ohio	Union Gas and Electric Co.
8	Fargo clay loam	Fargo, N. Dak	Union Light, Heat and Power Co.
9	Genesee silt loam	Sidney, Ohio	Tide Water Pipe Line Co., Ltd.
10	Gloucester sandy loam	Middleboro, Mass	Town of Middleboro.
11	Hagerstown loam	Baltimore, Md	Department of Public Works.
12	Hanford fine sandy loam.	Los Angeles, Calif	Southern Calif. Gas Co.
13	Hanford very fine sandy loam.	Bakersfield, Calif	San Joaquin Light and Power Corp.
14	Hemstead silt loam	St. Paul, Minn	Northern States Power Co.
15	Houston black clay	San Antonio, Tex	San Antonio Public Service Co.
16	Kalmia fine sandy loam	Mobile, Ala	City of Mobile.
17	Keyport loam	Alexandria, Va	Alexandria Water Co.
18	Knox silt loam	Omaha, Nebr	Omaha and Council Bluffs Electrolysis Committee.
19	Lindley silt loam	Des Moines, Iowa	Des Moines Gas Co.
20	Mahoning silt loam	Cleveland, Ohio	Department of Public Utilities.
22	Memphis silt loam	Memphis, Tenn	Board of Water Commissioners.
23	Merced silt loam	Buttonwillow, Calif	San Joaquin Light and Power Corp.
24	Merrimac gravelly sandy loam.	Norwood, Mass	Boston Consolidated Gas Co.
25	Miami clay loam	Milwaukee, Wis	Department of Public Works.
26	Miami silt loam	Springfield, Ohio	City of Springfield.
27	Miller clay	Bunkie, La	Standard Pipe Line Co.
28	Montezuma clay adobe	San Diego, Calif	San Diego Consolidated Gas and Electric Co.
29	Muck	New Orleans, La	Sewerage and Water Board.
30	Muscatine silt loam	Davenport, Iowa	United Light and Power Engineering and Construction Co.
31	Norfolk sand	Jacksonville, Fla	City Commission of Jacksonville.
32	Ontario loam	Rochester, N. Y	Department of Public Works.
33	Peat	Milwaukee, Wis	Milwaukee Gas Light Co.
34	Penn silt loam	Norristown, Pa	Philadelphia Electric Co.
35	Ramona loam	Los Angeles, Calif	Los Angeles Gas & Electric Co.
36	Ruston sandy loam	Meridian, Miss	Peoples Water and Gas Co.
37	St. Johns fine sand	Jacksonville, Fla	Jacksonville Gas Co.
38	Sassafras gravelly sandy loam.	Camden, N. J	Camden Water Dept.
39	Sassafras silt loam	Wilmington, Del	Delaware Power and Light Co.
40	Sharkey clay	New Orleans, La	New Orleans Public Service Co.
41	Summit silt loam	Kansas City, Mo	Kansas City Gas Co.

[2] I. A. Denison, *Electrolytic measurement of the corrosiveness of soils.* J. Research NBS **17**, 363 (1936) RP918, 5¢.

[3] I. A. Denison, *Methods for determining the total acidity of soils.* BS J. Research **10**, 413 (1933) RP539, 5¢.

TABLE 1.—*Identification of soils*—Continued

Soil	Soil type	Location	Cooperating organization
42	Susquehanna clay	Meridian, Miss	City of Meridian.
43	Tidal marsh	Elizabeth, N. J	Standard Oil Development Co.
44	Wabash silt loam	Omaha, Nebr	Omaha and Council Bluffs Electrolysis Committee.
45	Unidentified alkali soil	Casper, Wyo	Stanolind Oil and Gas Co.
46	Unidentified sandy loam	Denver, Colo	Public Service Co. of Colo.
47	Unidentified silt loam	Salt Lake City, Utah	Mountain Fuel Supply Co.
51	Acadia clay	Spindletop, Tex	Sinclair Prairie Pipe Line Co. of Tex.
53	Cecil clay loam	Atlanta, Ga	Department of Public Works.
54	Fairmount silt loam	Cincinnati, Ohio	Union Gas and Electric Co.
55	Hagerstown loam	Baltimore, Md	Bureau of Water Supply.
56	Lake Charles clay	El Vista, Tex	Gulf Pipe Line Co.
57	Merced clay adobe	Tranquillity, Calif	Standard Oil Co. of California.
58	Muck	New Orleans, La	Sewerage and Water Board.
59	Peat	Kalamazoo, Mich	Department of Public Utilities.
60	do	Plymouth, Ohio	Ohio Fuel Gas Co.
61	Sharkey clay	New Orleans, La	New Orleans Public Service Co.
62	Susquehanna clay	Meridian, Miss	City of Meridian.
63	Tidal marsh	Charleston, S. C	Commissioners of Public Works.
64	Unidentified alkali soil	Cholame Flats, Calif	Shell Oil Co.
65	do	Wilmington, Calif	Do.
66	Mohave sandy loam	Phoenix, Ariz	City Water Department.
67	Cinders	Milwaukee, Wis	Milwaukee Gas Light Co.

TABLE 2.—*Properties of soils* [a] *in the National Bureau of Standards soil-corrosion investigation*

(mg-eq = milligram equivalent)

A=Alkaline.
C=Not determined.
G=Good; *F*=Fair; *P*=Poor; *VP*= Very poor.

Soil [b]	Soil type	Mean temperature [c]	Annual precipitation [c]	Internal drainage of test site	Moisture equivalent	pH	Total acidity mg-eq per 100 g of soil	Resistivity at 60° F	Composition of water extract mg-eq per 100 g of soil						
									Na+K as Na	Ca	Mg	CO_3	HCO_3	Cl	SO_4
		°F	*Inches*		%			ohm-cm							
51	Acadia clay	69	49	*P*	47.1	6.2	13.2	190	10.27	15.55	5.03	0.00	0.56	5.75	22.00
52	Alkali knoll	69	47	*P*	54.8	8.8	*A*	234	4.20	.33	.18	.52	1.36	1.33	1.26
1	Allis silt loam	49.2	33.8	*P*	28.6	7.0	11.4	1,215	.72	.25	.43	.00	.09	.09	.83
2	Bell clay	65.5	36.2	*P*	37.6	7.3	3.5	684	.28	1.09	.13	.00	1.18	.04	.18
101	Billings silt loam	52.0	8.8	*F*	30.0	7.3	*A*	261	5.21	19.24	1.43	.00	.66	1.56	22.48
102	——do	52.0	8.8	*F*	20.4	7.3	*A*	103	22.63	16.56	3.85	.00	.56	4.67	36.82
103	——do	52.0	8.8	*F*	30.6	7.3	*A*	81	22.01	13.32	2.00	.00	.18	11.09	25.70
104	Cecil clay	60.2	46.1	*G*	34.1	4.6	11.0	8,500							
3	Cecil clay loam	61.2	48.3	*G*	29.1	5.2	11.5	30,000							
53	——do	61.2	48.3	*G*	33.7	4.6	9.6	17,794							
105	——do	64.2	44.5	*G*	34.2	4.8	12.9	28,000							
106	——do	60	46	*G*	38.8	4.8	12.8	25,000							
107	Cecil fine sandy loam	60.1	46.3	*G*	29.6	4.8	11.8	54,400							
108	Cecil gravelly loam	61.2	48.3	*G*	34.3	4.9	11.2	44,400							
4	Chester loam	54	40	*F*	22.2	5.6	7.6	6,670							
67	Cinders	46.1	30.1	*VP*	11.1	8.0	*A*	455	.77	3.03	.53	.00	.55	.08	2.89
5	Dublin clay adobe	56.4	23.4	*P*	28.8	7.0	6.5	1,346	.93	.48	.10	.00	.69	.03	.25
6	Everett gravelly sandy loam	51.0	34.0	*G*	12.2	5.9	12.8	45,100							
54	Fairmount silt loam	53.2	38.6	*P*	26.1	7.0	3.5	886	.59	10.10	.59	.00	.70	.08	9.05
8	Fargo clay loam	39	21	*P*	37.0	7.6	*A*	350	1.42	1.72	2.55	.00	.71	.01	4.43
109	Fresno fine sandy loam	63	9	*P*	18.6	8.4	*A*	497	2.62	.07	.10	.31	.59	1.56	.48
110	——do	63	9	*P*	18.4	10.2	*A*	531	3.53	.07	.12	1.49	1.07	.79	.25
111	——do	63	9	*P*	22.1	7.3	*A*	51	41.55	16.21	.44	.00	.58	34.58	23.41
9	Genesee silt loam	51.2	39.0	*P*	24.8	6.8	7.2	2,820							
10	Gloucester sandy loam	50	41	*F*	13.0	6.6	3.6	7,460							
11	Hagerstown loam	55.4	42.6	*G*	32.0	5.3	10.8	11,000							
55	——do	55.4	42.6	*G*	32.0	5.8	10.9	5,213							
12	Hanford fine sandy loam	62.4	15.2	*F*	12.4	7.1	2.5	3,190	.39	.50	.16	.00	.40	.00	.14
13	Hanford very fine sandy loam	64.6	5.6	*F*	21.7	9.5	*A*	290	6.23	.09	.13	.00	1.12	1.64	3.76
14	Hempstead silt loam	44.2	27.2	*F*	17.2	6.2	5.6	3,520							
15	Houston black clay	68.9	27.2	*P*	51.4	7.5	5.0	489	2.18	.88	.20	.00	2.00	.13	.73
112	Imperial clay	71	2	*P*	30.2	7.4	*A*	176	22.18	14.69	1.70	.00	.00	1.00	36.00
113	——do	71	2	*P*											

15	Houston black clay	66.9	27.2	P	51.4	7.5	5.0	489	2.18	.88	.20	.00	2.00	.13	.73
113	Imperial clay	71	2	F	30.2	7.4	A	176	22.18	14.09	1.29	.00	.36	10.94	25.98
119	do	71	2	F	34.6	7.4	A	92	9.56	.84	.51	.00	.63	6.26	4.06
16	Kalmia fine sandy loam	67.3	61.6	F	22.2	4.4	11.8	8,290							
17	Keyport loam	55	42	P	30.8	4.5	19.1	5,980							
18	Knox silt loam	50.6	27.8	G	28.4	7.3	1.4	1,410	.27	.63	.20	.00	.94	.00	.25
56	Lake Charles clay	69	49	P	28.7	7.1	4.5	406	3.12	.69	.47	.00	.80	1.59	3.04
114	do	69	49	P	35.8	7.1	C	320	2.65	.68	.26	.00	.77	1.84	.93
19	Lindley silt loam	49.5	32.0	G	28.4	4.6	10.9	1,970	.38	.32	.41	.00	.16	.03	.46
20	Mahoning silt loam	49.2	33.8	P	22.4	7.5	1.5	2,870	.25	.48	.20	.00	.51	.00	.15
21	Marshall silt loam	54.4	37.1	F	31.2	6.2	9.5	2,370							
22	Memphis silt loam	61.6	47.7	G	28.4	4.9	9.7	5,150							
115	do	65.6	51.9	G	25.7	6.9	4.7	3,450							
116	Merced clay	63.4	8.1	F	39.7	9.2	A	320	9.30	.33	.18	4.60	2.10	1.17	1.57
57	Merced clay adobe	63	8	P	40.9	7.7	A	128	23.40	13.50	4.51	.00	.34	1.15	37.50
117	Merced clay loam adobe	63	8	P	51.8	8.5	A	106	36.19	14.66	.83	.00	1.55	2.89	46.53
25	Merced silt loam	65	6	P	24.7	9.4	A	278	8.38	.38	.22	.02	1.87	1.12	5.57
24	Merrimac gravelly, sandy loam	50	41	G	13.0	4.5	12.6	11,400							
25	Miami clay loam	46.1	30.1	F	25.8	7.2	4.7	1,780	.23	.70	.41	.00	1.01	.03	.10
26	Miami silt loam	53	37	G	16.4	7.3	2.6	2,980	.27	.50	.31	.00	.70	.03	.12
27	Miller clay	67	56	P	42.6	6.6	3.7	570	.53	1.86	1.12	.00	2.00	.08	1.54
66	Mohave sandy loam	69.7	7.8	G	16.5	8.7	A	232	6.55	.51	.18	.00	.73	2.77	2.97
28	Montezuma clay adobe	61.0	10.3	P	24.6	6.8	C	408	1.50	.06	.18	.00	.12	.99	.89
29	Muck	69.3	57.4	VP	34.5	4.2	28.1	1,270	2.15	1.92	1.55	.00	.00	1.69	2.30
58	do	69.3	57.4	VP	57.8	4.0	79.3	712	2.03	2.23	1.29	.00	.00	.47	2.54
30	Muscatine silt loam	49.9	32.1	P	29.4	7.0	2.6	1,300	.32	.65	.40	.00	.71	.09	.24
118	Niland gravelly sand	71	2	F	6.1	7.3	A	273	4.30	1.03	.64	.00	.20	5.01	.86
31	Norfolk sand	69.3	47.4	G	2.8	4.7	1.8	20,500							
120	do	67.7	57.9	G	4.4	5.7	1.3	34,400							
121	do	71.8	49.4	G	3.0	4.8	1.2	16,400							
119	Norfolk sandy loam	64.2	44.5	G	24.1	4.7	9.7	10,800							
32	Ontario loam	47.6	32.8	G	17.8	7.3	0.5	5,700	.23	.70	.12	.00	.73	.01	.42
122	Panoche clay loam	63	6.4	F	30.0	7.4	A	552	2.32	.05	.26	.00	.70	.07	1.40
53	Peat	46.1	30.1	VP	72.8	6.8	36.0	800	1.52	7.30	4.06	.00	C	2.27	2.13
59	do	49	31	VP	43.6	5.5	33.3	1,659	1.03	3.08	2.70	.00	.00	3.47	1.04
60	do	49	37	VP	43.4	2.6	297.4	218	2.91	10.95	2.86	.00	.00	.00	56.70
34	Penn silt loam	54	40	F	23.4	6.7	7.0	4,900							
35	Ramona loam	62.4	15.2	G	18.0	7.3	5.7	2,060	.68	.68	.49	.00	1.10	.06	.35
36	Ruston sandy loam	64.0	53.0	G	13.8	4.5	4.6	11,200							
37	St. Johns fine sand	69.3	47.4	P	7.0	3.8	15.3	11,200							

[a] Measurements and determinations by I. A. Denison and R. B. Hobbs.
[b] For locations of soils see table 1.
[c] Data furnished by U. S. Weather Bureau. Values with no figures to the right of the decimal point are for some nearby city

TABLE 2.—*Properties of soils in the National Bureau of Standards soil-corrosion investigation*—Continued

Soil [b]	Soil type	Mean temperature	Annual precipitation	Internal drainage of test site	Moisture equivalent	pH	Total acidity mg-eq per 100 g of soil	Resistivity at 60° F	Composition of water extract mg-eq per 100 g of soil						
									Na+K as Na	Ca	Mg	CO_3	HCO_3	Cl	SO_4
		°F			%			ohm-cm							
38	Sassafras gravelly sandy loam	54	40	G	3.0	4.5	1.7	38,600							
39	Sassafras silt loam	54	40	P	24.2	5.6	6.6	7,440							
40	Sharkey clay	69.3	57.4	P	33.0	6.0	9.4	970	0.56	0.58	0.44	0.00	0.93	0.07	0.28
61	do	69.3	57.4	P	30.8	5.9	8.6	943	.73	.68	.33	.00	.71	.10	.91
41	Summit silt loam	54.4	37.1	F	33.1	5.5	11.0	1,320	.30	.54	.36	.00	.78	.04	.46
42	Susquehanna clay	64.0	53.0	P	34.8	4.7	28.2	13,700							
62	do	64.0	53.0	P	34.6	4.1	24.2	6,922							
123	do	65.8	43.4	P	37.6	4.1	21.9	6,840							
124	Susquehanna silt loam	66.0	42.7	P	36.0	4.4	28.1	1,160							
125	Susquehanna fine sandy loam	65.8	43.4	P	37.2	3.9	28.3	5,770							
43	Tidal marsh	52	43	VP	55.4	3.1	36.8	60	45.10	5.17	9.45	.00	.00	43.30	37.00
63	do	66.0	45.2	VP	46.7	2.9	100.2	84	33.60	6.85	4.00	.00	.00	12.70	36.60
44	Wabash silt loam	50.6	27.8	G	31.2	5.8	8.8	1,000	1.05	1.08	.66	.00	1.97	.82	.41
	UNIDENTIFIED SOILS														
45	Alkali soil	47.2	15.3	P	14.8	7.4	A	263	8.15	3.70	.70	.00	.24	.18	11.98
46	Sandy loam	50.0	14.1	G	7.6	7.0	C	1,500							
7	Silt loam [d]	53.2	38.6	P	34.3	4.4	29.8	2,120							
47	do	51.6	16.1	P	25.7	7.6	3.0	1,770	.67	.72	.39	.00	.88	.06	.48
64	Alkali soil	58	16	VP	41.1	8.3	A	62	28.10	2.29	.76	.00	.89	28.80	.26
65	do	62.4	15.2	F	26.4	7.2	A	148	7.65	12.40	2.20	.00	1.30	6.05	16.90

[d] Previously classified erroneously as Fairmount silt loam.

III. METALLIC COATINGS

1. LEAD-COATED PIPE

Lead-coated pipe was exposed to corrosion at various test sites on three occasions. The first of these was in 1924 when specimens of 1½-inch lead-coated steel pipe 6 inches long were placed in 47 soils.

Two years after the first lead-coated specimens were buried, specimens of steel pipe coated by a hot-dip process by another manufacturer were placed in seven soils.

A third test of lead-coated steel pipe was begun in 1932. The specimens were prepared by the manufacturer of the specimens buried in 1924. This coating consists of approximately 98 percent of lead and 2 percent of tin, bonded to the base metal by a third element or bonding agent.

The thickness of the lead coatings was determined using the chord method.[4] The results of these measurements are given in table 3. The three lead coatings all have about the same average thickness (1 to 1.5 mils), and they all show wide variations in thickness from point to point.

TABLE 3.—*Dimensions of and thickness of coating on lead-coated pipe specimens*

Dimensions of specimens (in.)	1½ by 6	2 by 17	1½ by 13
Date of burial	1924	1926	1932
Number of measurements	8	9	12
Average thickness (mils)	1.05	1.18	1.44
Minimum thickness (mils)	2.50	1.96	2.97
	0.30	0.82	0.50

Table 4 gives the average rates of loss of weight and of maximum penetration for 10-year-old specimens buried in 1924. The table also shows the corresponding rates of corrosion for unprotected steel pipe and lead cable sheath.

Only in Ramona loam were the specimens free from pits. In Dublin clay adobe, the coated specimens were worse than the uncoated both with respect to loss of weight and penetration. In 13 of the 34 soils for which comparisons can be made, the rates of maximum penetration were greater for the coated specimens. Severe pitting of lead-coated specimens occurred in several soils in which commercial lead cable sheath was attacked but little.

The data on rates of corrosion of lead cable sheath show that, in general, corrosion is most severe in the absence of oxygen and salts (especially sulphates) either of which would precipitate a protective layer of corrosion products on the lead. However, in all soils the rate of corrosion is great enough to penetrate the lead coating somewhere, even if the coating were originally free of pinholes. After it is exposed, the rate of penetration of the steel depends largely upon the rate at which bare steel is attacked. In soils of low resistance, the lead accelerates the rate of corrosion if the coating is punctured. The places where the lead coating seems to be most effective in reducing the rates of corrosion and pitting are well-drained soils of very high resistivity. In such soils the penetration of the bare ferrous pipe wall practically stops after a few years.

[4] W. Blum and A. Brenner, *Mesle's chord method for measuring the thickness of metallic coatings.* J. Research NBS 16, 171 (1936) RP866, 5¢.

TABLE 4.—*Corrosion of 1½- by 6-inch lead-coated pipe exposed for approximately 10 years*

Soil	Soil type	Rates of loss (oz/ft²/yr)			Rates of maximum penetration (mils/yr)		
		Lead-coated steel	Bare steel [1]	Lead cable sheath [1]	Lead-coated steel	Bare steel	Lead cable sheath
1	Allis silt loam	0.529	0.80	0.173	11.9	5.8	3.1
2	Bell clay	.102	.49	.067	4.0	6.7	1.3
3	Cecil clay loam	.066	.43	.059	3.6	4.5	1.4
4	Chester loam	.239	.52	.177	7.0	6.8	4.0
5	Dublin clay adobe	.597	.45	.135	6.9	3.1	3.3
6	Everett gravelly, sandy loam	.006	.08	.025	2.0	1.4	0.3
7	Unidentified silt loam	.207	.37	----------	7.0	2.5	----------
9	Genesee silt loam	.080	.43	----------	5.0	4.5	----------
10	Gloucester sandy loam	.163	.36	.088	6.5	3.2	1.2
11	Hagerstown loam	.071	.16	.034	3.4	4.9	1.2
13	Hanford very fine sandy loam	.064	----------	----------	5.4	----------	----------
14	Hempstead silt loam	.036	.39	.049	4.2	7.1	1.7
15	Houston black clay	.052	.65	.036	3.2	4.4	2.2
17	Keyport loam	.379	.77	.028	4.7	3.3	1.7
18	Knox silt loam	.046	.23	.016	4.6	3.2	1.1
20	Mahoning silt loam	.224	.52	.268	5.3	5.5	4.1
22	Memphis silt loam	.192	.61	.085	7.3	6.6	1.3
24	Merrimac gravelly, sandy loam	.033	.12	.015	2.2	2.1	1.5
27	Miller clay	.231	.63	.067	5.6	4.9	2.4
28	Montezuma clay adobe	.314	1.75	.069	7.8	15.1	0.9
29	Muck	.689	1.61	.343	6.3	12.0	.9
31	Norfolk sand	.028	.22	.022	1.5	2.5	.5
32	Ontario loam	.072	.32	.028	5.2	4.3	1.5
33	Peat	.537	1.22	----------	7.7	8.9	----------
35	Ramona loam	.011	.09	.017	(2)	0.4	2.3
36	Ruston sandy loam	.032	.24	.032	1.8	3.9	1.1
37	St. Johns fine sand	.202	.58	----------	6.4	5.6	----------
38	Sassafras gravelly, sandy loam	.053	.22	.025	3.4	2.5	1.7
40	Sharkey clay	.191	.56	----------	6.2	6.6	----------
41	Summit silt loam	.051	.45	.039	5.8	7.6	1.5
42	Susquehanna clay	.092	.95	----------	4.6	7.1	----------
43	Tidal marsh	.726	1.47	.019	18.8	8.7	1.0
45	Unidentified alkali soil	.198	.79	.021	9.2	6.9	1.7
46	Unidentified sandy loam	.033	.37	.015	4.5	8.8	1.0
47	Unidentified silt loam	.184	.23	.122	6.1	2.4	5.7

[1] Bessemer steel pipe 1½ by 6 inches and commercial lead cable sheath in sheets 20¾ by 3½ by 0.112 inch removed from sites at the same time the lead-coated specimens were removed, were buried, in most cases, 1 or 2 years longer. The figures given are the averages from 2 specimens in the case of the steel and 1 specimen in the case of the lead sheath. The penetration of the sheath was determined by averaging 2 pits, each of which was the deepest on 1 side of the specimen. These pits were, of course, somewhat deeper than would be expected on specimens of the same exposed area as that of the pipe.

[2] No pits.

Table 5 shows the rates of corrosion of the lead-coated specimens buried in 1926, together with the corresponding rates for steel specimens of the same dimensions.

Table 6 gives the data on the specimens buried in 1932 and removed in 1934. It will be noted that in 5 of the 14 soils the lead-coated specimens developed deeper pits in 2 years than did the bare specimens. All of the specimens developed measurable pits, and large holes were found in the specimens exposed to cinders.

TABLE 5.—*Corrosion of 2 by 17 inches lead-coated steel pipe exposed approximately 8 years*

Soil	Soil type	Rate of loss (oz/ft.²/yr)		Rate of penetration (mils/yr)	
		Lead-coated steel	Bare steel [a]	Lead-coated steel	Bare steel
13	Hanford very fine sandy loam	0.18	1.70	6.5	19.3
24	Merrimac gravelly, sandy loam	.08	0.21	3.3	3.7
28	Montezuma clay adobe	1.09		9.1	
29	Muck	0.61	1.21	7.8	10.5
42	Susquehanna clay	.44	0.89	7.4	8.8
43	Tidal marsh	[b].77	.86	[b]18.0	10.8
45	Unidentified alkali (Casper, Wyo.)	1.27	2.64	10.1	16.6

[a] The data in this column are from specimens of bare Bessemer steel of the same dimensions as the lead-coated specimens and which were buried and removed at the same times. Those in soil 24 were of copper-bearing steel.

[b] Of the 4 lead-coated specimens in soil 43, 3 were punctured, and since the ends of the specimens were closed, it was impossible to clean them in order to determine the weight lost. The figures given with respect to both rate of loss of weight and penetration are for the remaining specimen. These specimens were of 0.154-inch wall thickness.

TABLE 6.—*Corrosion of 1½- by 13-inch lead-coated steel pipe exposed approximately 2 years*

Soil	Soil type	Rates of loss (oz/ft²/yr)		Rates of maximum penetration (mils/yr)	
		Lead-coated steel	Bare steel [1]	Lead-coated steel	Bare steel [1]
51	Acadia clay	2.72	3.75	27.3	41.4
53	Cecil clay loam	0.40	1.37	18.4	18.9
55	Hagerstown loam	.25	1.28	11.9	21.7
56	Lake Charles clay	.53	2.03	28.7	9.8
57	Merced clay adobe	.24	2.33	11.3	16.8
58	Muck	.87	1.85	14.8	9.0
60	Peat	1.59	3.24	20.8	19.3
61	Sharkey clay	0.38	0.86	21.6	11.1
62	Susquehanna clay	.41	2.12	17.9	32.1
63	Tidal marsh	.01	1.88	7.8	7.4
64	Salinas loamy sand	.19	6.62	18.6	68.3
65	Alkali soil (Wilmington, Calif.)	.20	3.87	14.7	20.7
66	Mohave sandy loam	.41	4.02	19.0	34.4
67	Cinders	16.66	10.65	65.3	76.2

[1] Low-carbon steel tube 2 by 10 inches buried and removed at the same times as the lead-coated pipe.

It is of interest to compare the corrosion-resisting properties of the three coatings developed at different times in three types of soil. Such a comparison is shown in table 7.

Figure 1 shows the appearance of the specimens after exposures of 2, 6, and 8 years. It is evident that no marked improvement in the resistance to soil corrosion of this type of coating has been made since the first specimens were buried.

It is believed that these data justify the conclusion that lead coatings in general are not suitable for protecting steel pipe against soil corrosion. In the early stages, lead coating reduces corrosion. However, after the coating is penetrated, the rate of penetration of the steel is often accelerated, so that in many cases the pipe wall will be penetrated earlier on the lead-coated than on the bare steel pipe.

TABLE 7.—*Comparison of corrodibility of three varieties of lead-coated pipe exposed 2 to 4 years to three soils*

Type	Lead-coated Bessemer steel			
	No. 1 [a]	No. 2 [b]	No. 3 [c]	Bare Bessemer steel [d]
RATES OF LOSS OF WEIGHT (oz/ft²/yr)				
Muck	0.88	0.85	0.87	1.88
Susquehanna clay	.14	.81	.41	2.12
Tidal marsh	.41	.69	.01	1.88
RATES OF MAXIMUM PENETRATION (mils/yr)				
Muck	[e]21.3	[f]8.7	[f]14.8	[f]9.0
Susquehanna clay	19.7	14.0	17.9	32.1
Tidal marsh	52.2	24.2	7.8	7.4

[a] 1¼- by 6-inch coated steel pipe exposed 2 to 2½ years to soils *29*, *42*, and *43*.
[b] 2- by 17-inch coated steel pipe exposed about 4 years to soils *29*, *42*, and *45*.
[c] 1¼- by 13-inch coated steel pipe exposed 2 years to soils *58*, *62*, and *63*.
[d] 2- by 10-inch bare steel tube exposed 2 years to soils *58*, *62*, and *63*.
[e] Single deepest pit on 2 specimens having combined exposed area equal to that of 1 pipe 1¼ by 10 inches.
[f] Average of the 2 deepest pits, 1 from each specimen.

2. ALUMINUM (CALORIZED)

A calorized coating is an alloy of aluminum with the base metal. It was developed primarily for the purpose of preventing scaling when the metal is subjected to high temperatures. The aluminum oxide, which develops on the surface of calorized materials, was considered as a possible protection against soil corrosion. There are two processes of calorizing, one known as the powder or dry process, and the other as the dip or wet process. Specimens of pipe calorized by each process were placed in seven soils in 1924. Since it seemed inadvisable to stamp numbers on these specimens or to attach tags by wires which might cause galvanic corrosion, the specimens were identified by their positions in the trenches. This has resulted in the loss of identification of some of the specimens. Table 8 gives the rates of corrosion of the calorized specimens, together with the corresponding data for unprotected steel.

TABLE 8.—*Corrosion of calorized steel pipe exposed approximately 10 years*

Soil	Soil type	Rates of loss of weight [1] (oz/ft²/yr)			Rates of maximum penetration [1] (mils/yr)		
		Dry calorized	Wet calorized	Bare steel [2]	Dry calorized	Wet calorized	Bare steel [2]
13	Hanford very fine sandy loam	0.137	0.087	1.24	3.4	4.4	13.0
24	Merrimac gravelly, sandy loam	.019	.013	0.12	2.4	3.2	2.1
28	Montezuma clay adobe	.437		1.75	5.5		15.1
29	Muck	.250	.458	1.39	3.4	7.8	9.2
42	Susquehanna clay	.452	.088	1.25	7.0	4.2	9.2
43	Tidal marsh	.861	.434	1.72	3.1	3.4	7.4
45	Alkali soil (Casper, Wyo.)	.712	.184	1.23	3.4	4.4	11.9

[1] Average of 2 specimens.
[2] Rates for unprotected Bessemer steel specimens of similar area which were exposed, except in the case of soil *13*, for a similar period. The data presented for bare steel in soil *13* are for specimens exposed only 6 years, there being no data available for a longer period.

Research Paper 982
Journal of Research of the National Bureau of Standards

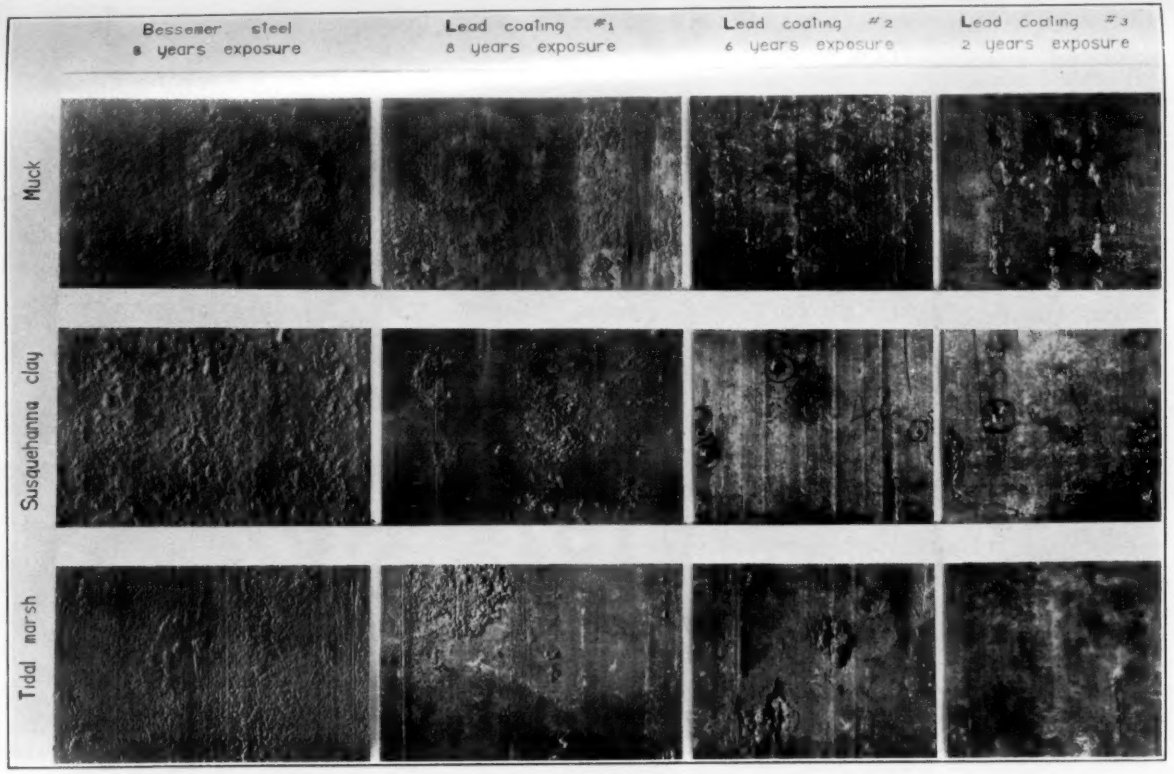

FIGURE 1.—*Steel pipe and three varieties of lead coatings removed from three soils in 1934.*

The specimens are 5 inches high.

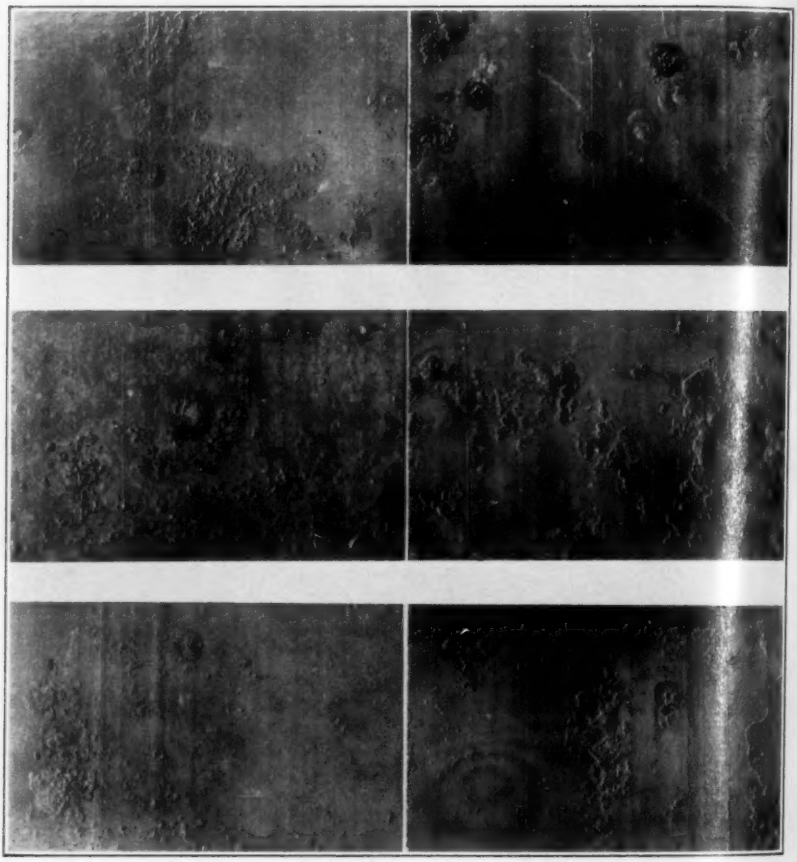

FIGURE 2.—*Powder- (on the left) and dip- (on the right) calorized specimens exposed for 10 years to Hanford very fine sandy loam containing black alkali (carbonates) at top; muck (center); and Susquehanna clay (bottom).*

The specimens are 5 inches high.

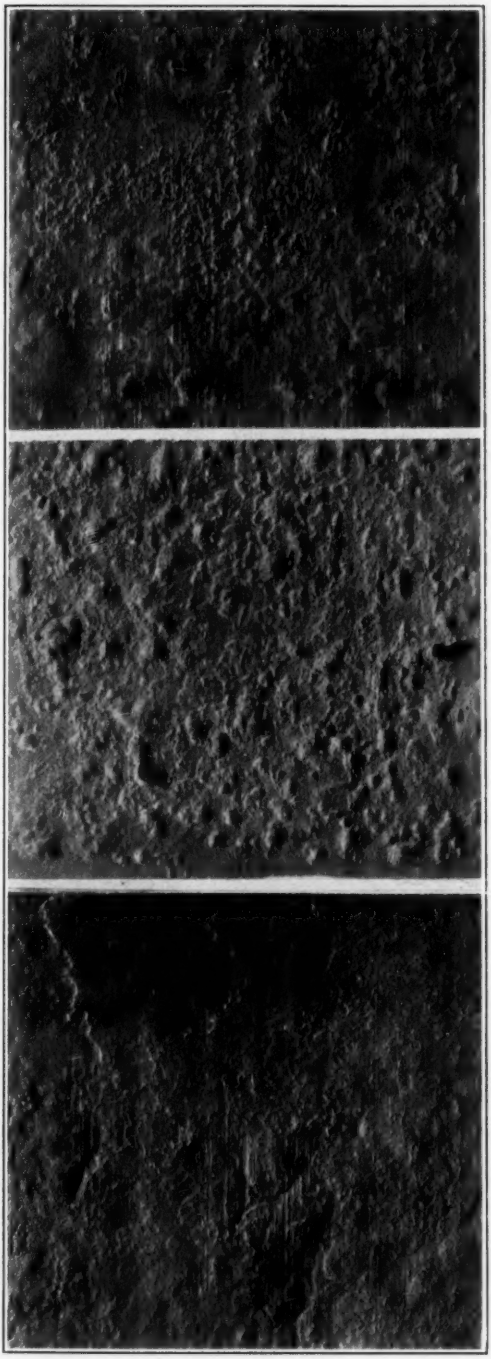

FIGURE 3.—*Bessimer steel specimens exposed with the calorized specimens in figure 2.*

Hanford very fine sandy loam (top); muck (center); Susquehanna clay (bottom). The specimens are 5 inches high.

In all cases the calorized specimens lost weight and, with one exception, were pitted at a lower rate than the unprotected pipe in the same soils. In five of the six soils the powder-calorized pipe was pitted at a lower maximum rate than the dip-calorized pipe, while in five of six soils the dip-calorized pipe lost less weight than the powder-calorized pipe. It is thus apparent that the powder-calorized coating was more effective in reducing pitting, although it allowed a greater loss of weight than the dip-calorized coating.[5]

The thickness of the coating on both types of calorized pipes was measured in several places, using the chord method,[6] potassium ferrocyanide and copper sulphate being applied to distinguish the alloy boundary. The thickness of the coating on both kinds of calorized pipe was found to be reasonably uniform. The thickness of the powder-calorized coating was 2 mils and that of the dip-calorized was 11 mils.

It is evident from table 8 that although, on the whole, calorizing made the pipe more resistant to soil corrosion, the process as applied to the specimens did not prevent pitting in any soil. The rate of pitting and loss of weight are usually high in poorly drained, corrosive soils where the use of a good coating would be economical. The appearance of the calorized specimens from three widely different soils is shown in figure 2. Unprotected steel specimens exposed to the same soils for the same times are shown in figure 3. While these photographs have been selected to show the appearance of more or less typical specimens, they are not presented as the basis for general conclusions.

3. ZINC (GALVANIZED)

The tests of galvanized ferrous pipe and sheet were undertaken in order to determine the effectiveness of various thicknesses of this type of coating in withstanding soil action, and to ascertain whether or not one base material was superior to another when the same weight of zinc was applied to each.

Galvanized iron prepared by the hot-dip process includes an outer layer of nearly pure zinc, a middle zone of one or more alloys of zinc and iron, and finally, the metal to which the zinc was applied. The thickness of the alloy layer depends upon the methods used in galvanizing, and to some extent on the character of the base metal. It is not practicable to apply an exact amount of zinc or to apply the zinc as a perfectly uniform coating by the hot-dip process as used commercially[7][8]. For these reasons, and because of nonuniform soil conditions, some dispersion of the data for what is nominally the same weight of coating is to be expected.

It is evident from the statements above that the determination of the effect of each factor in the corrosion of galvanized specimens under field conditions would be very difficult, if not impossible, even with a very large number of specimens. From the available data, it is possible to draw general conclusions only. These conclusions are valid only for the period covered by the experiments.

[5] For a description of calorizing processes, see H. S. Rawdon, Protective Metallic Coatings. (The Chemical Catalog Co., New York, N. Y.)
[6] See footnote 5.
[7] H. S. Rawdon, Protective Metallic Coatings. (The Chemical Catalog Co., New York, N. Y., 1928.)
[8] E. C. Groesbeck and Wm. A. Tucker, *Accelerated laboratory corrosion test methods for zinc-coated steel.* BS J. Research 1, 255 (1928) RP10.

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[8] E. C. Groesbeck and Wm. A. Tucker, *Accelerated laboratory corrosion test methods for zinc-coated steel.* BS J. Research 1, 255 (1928) RP10.

The first test of galvanized pipe was started in 1922 when two 24-inch specimens of 2-inch galvanized steel pipe were placed in 30 soils. One of these specimens was removed from each soil in 1926, and the other specimens were removed in 1934. The specimens were not weighed.

In 1924, specimens of galvanized pipe and sheet were placed in 46 soils. In seven of these soils specimens having different weights of coatings were also buried.

Table 9 gives the corrosion data on pipe and sheets carrying nominal 2-ounce coatings. In the case of pipes, this is the nominal weight of the coating on 1 square foot of the outside surface of the pipe, while in the case of sheet metal it refers to the weight of coating per square foot of sheet and is, therefore, twice the weight of the coating on 1 square foot of surface. To avoid confusion, the weights of coating given near the top of the table are all expressed in ounces of zinc per square foot of surface. Although all specimens listed in table 9 carried the same nominal weight of coating, the actual weights differed considerably, and the uniformity of the coating on the same kind of specimens also varied.[9]

Table 9 shows also the rates of corrosion of steel pipe for those soils for which data on this material for the same period of exposure are available. To make the comparison of the galvanized and bare materials easier, the ratio of the rates of corrosion of the two materials is also shown. A low ratio indicates that the coating was relatively effective.

The composition of the steel to which the coating was applied has been given in Technologic Paper 368.[10] Results of early examinations of coatings will be found in that paper, as well as in Research Papers 359 [11] and 638.[12]

The specimens were cleaned with warm water and a stiff fiber brush, and, in some cases, not all of the corrosion products were removed. The rates of loss of weight given in tables 9, 10, 11 are, therefore, somewhat less than they should be. They are, however, comparable with earlier data on specimens cleaned in the same way and give a good indication of the condition of the specimens.

In order to show the correlation between weight losses and the results of the 10-year inspections, the data in table 9 are given graphically in figure 4. The rates of loss of weight for each of the four materials are plotted on a logarithmic scale on separate lines, each point representing one specimen. The thick lines indicate the thickness of the coatings. The condition of each specimen, as judged by inspection and the weight of the coating, is shown in the figure. It can be seen that the various visual classifications are well grouped, with some overlapping. However, the weight losses do not arrange the specimens in exactly the same order as the inspection results and pit measurements. This lack of correlation is not due entirely to chance. In figure 5 the average rate of loss of weight of the three galvanized sheets is plotted against the average maxi-

[9] See footnotes 7 and 8, p. 371.

[10] K. H. Logan, S. P. Ewing, and C. D. Yoeman, *Bureau of Standards soil-corrosion studies: I. Soils, materials, and results of early observations.* Tech. Pap. BS **22**, 447 (1928) T368, 50c.

[11] K. H. Logan. *Soil-corrosion studies. Nonferrous metals and alloys, metallic coatings, and specially prepared ferrous pipes removed in 1930.* BS J. Research **7**, 585 (1931) RP359.

[12] K. H. Logan and R. H. Taylor. *Soil-corrosion studies, 1932. Rates of loss of weight and pitting of ferrous and nonferrous specimens and metallic protective coatings.* BS J. Research **12**, 112 (1934) RP638.

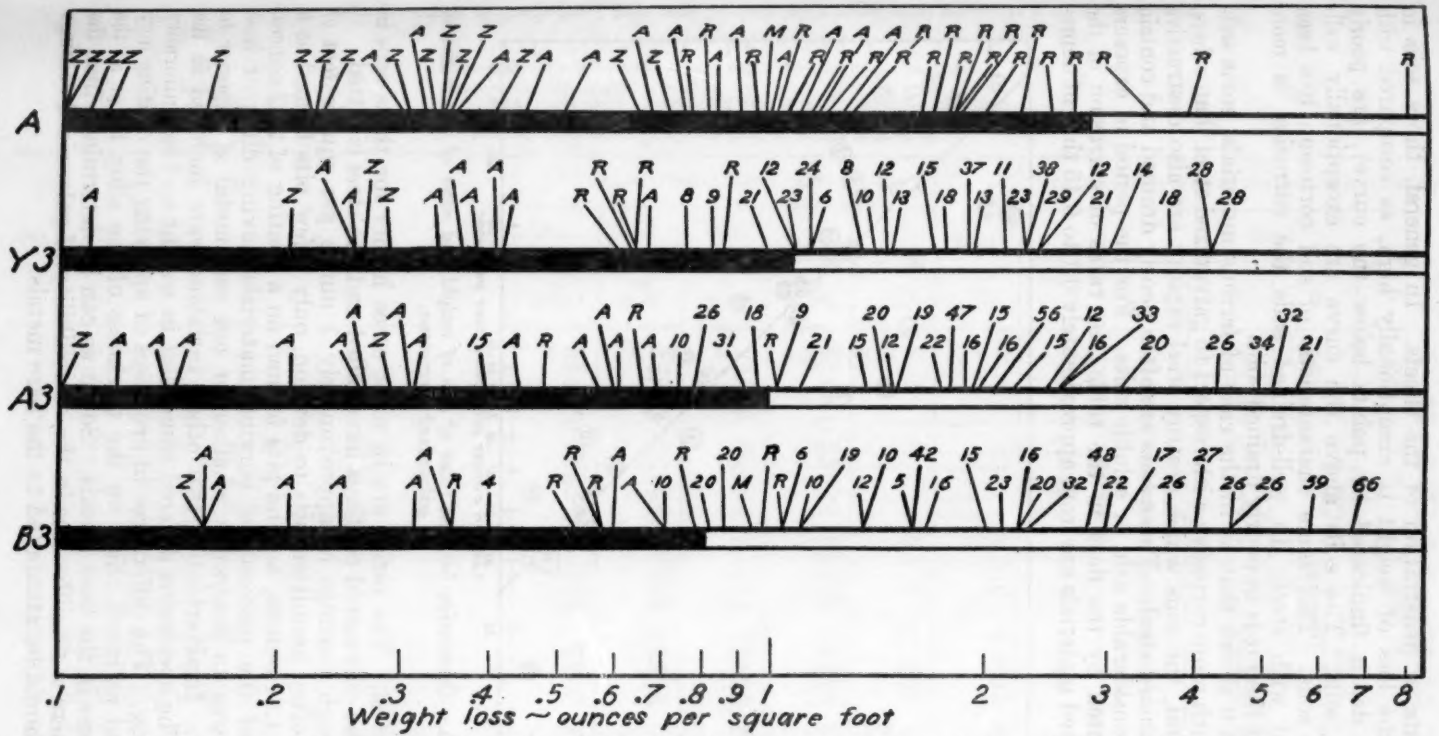

FIGURE 4.—*Correlation between losses of weight and condition of galvanized specimens as determined by inspection.*

The specimens were 10 years old. When figures appear they are the rates of penetration of the maximum pit, in mils per year. When letters appear they have the following meanings:

Z=Zinc continuous over specimen.
A=Blue or black alloy layer exposed over at least part of specimen.
R=Rusted or bare steel exposed.
M=Shallow metal attack; no pit as great as 10 mils total depth.

mum rate of penetration of the sheets. In general, those soils in which the loss of weight is exceptionally high, as compared with the pit depth (indicated by points below the curve), are poorly drained soils. The soils above the curve are exceptionally well-drained soils. This same characteristic of soil corrosion has been observed with steel. In well-drained soils the corrosion is more localized than it is in poorly drained soils.

Table 9 shows that as in the case of ferrous materials, some soils were much more corrosive with respect to galvanized steel than others. In general, the soils which destroy steel rapidly are also destructive to galvanized steel. These soils are often poorly drained and contain either considerable acid or soluble salts. For the period of exposure represented by the data in the table, the rates of corrosion of the galvanized materials are from approximately 0.1 to 0.45 that of unpro-

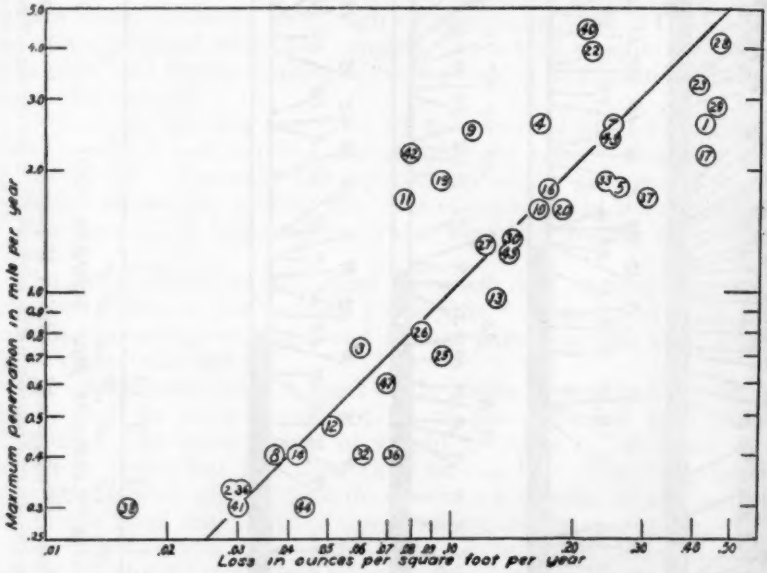

FIGURE 5.—*Correlation between rates of loss of weight and rates of penetration on galvanized specimens.*

tected steel. The ratios are in most cases higher for those soils in which the galvanized coatings have failed and the steel is pitted.

Although coatings of approximately 1 ounce per square foot of surface often permitted pits to develop, only a few pits formed on a coating 1.81 ounces, and no pits formed on a coating of 2.82 ounces.

One of the reasons for burying materials having different base metals was to determine whether or not one metal is superior to another. Inadvertently, two other variables were included in the test. The specimens differed somewhat in weight and in uniformity of coating. The differences in processes of applying the coating may have had as much effect on the thickness of the alloy layer as the differences in the base metals. So far as can be determined from the data, there is no difference in the corrodibility of galvanized coatings which should be attributed to the base metals.

TABLE 9.—*Corrosion of galvanized pipe and 16-gage steel sheet with nominal 2-ounce coatings*

[Average time buried 10 years]

The numbers in parentheses are the weights (oz/ft²) of the coatings.
Z=Zinc continuous over specimen.
A=Blue or black alloy layer exposed over at least a portion of specimen.
R=Rusted or bare steel exposed.
M=Shallow metal attack; no pit as great as 10 mils total depth.

Soil	Soil type	Rates of loss of weight (oz/ft²/yr)					Ratio [c]	Condition or rates of maximum penetration (mils/yr)				
		Pipe	Sheet			Bare [b]		Pipe *B* [d] (1.81)	Sheet			
		A (2.82) [a]	*A3* (0.99)	*B* (0.81)	*Y3* (1.07)				*A*	*A3*	*B*	*Y3*
1	Allis silt loam	0.274	0.433	0.449	0.418	0.957	0.41	2.5	*R*	2.6	2.6	2.8
2	Bell clay	.035	.044	.058	.029			*M*	*Z*	*A*	*R*	*Z*
3	Cecil clay loam	.041	.048	.071	.061	.393	.14	*M*	*Z*	*R*	1.0	*R*
4	Chester loam	.183	.174	.166	.193			*R*	*R*	2.2	1.6	1.3
5	Dublin clay adobe	.179	.246	.298	.241				*R*	1.2	2.2	1.2
6	Everett gravelly, sandy loam	.012	.027	.025	.009				*Z*	*A*	*A*	*Z*
7	Unidentified silt loam	.250	.257	.225	.290			*R*	*R*	1.6	1.6	2.1
8	Fargo clay loam	.073	.061	.053	.037	.522	.11	*R*	*Z*	*A*	*R*	*A*
9	Genesee silt loam	.116	.092	.082	.114			*R*	*A*	3.1	2.0	2.4
10	Gloucester sandy loam [e]	.121	.164	.161	.165			*A*	*R*	1.5	2.3	1.1
11	Hagerstown loam	.085	.040	.086	.109	.170	.47		*A*	1.5	2.0	1.2
12	Hanford fine sandy loam		.032	.094	.026			*A*		*A*	*M*	*A*
13	Hanford very fine sandy loam	[f].086	.219	.036	.135				*R*	1.5	*R*	0.8
14	Hempstead silt loam	.024	.031	.032	.064	.470	.08	*A*	*Z*	*A*	*A*	*R*
15	Houston black clay	.035	.029	.060	.021				*Z*	*Z*	*A*	*Z*
16	Kalmia fine sandy loam	.099	.145	.203	.177	.641	.24	*Z*	*M*	2.0	1.5	1.8
17	Keyport loam	.344	.558	.371	.368			*R*	*R*	2.1	2.6	1.8
19	Lindley silt loam	.065	.078	.110	.099	.314	.28	*A*	*Z*	2.6	1.9	2.1
20	Mahoning silt loam	.114	.197	.225	.146	.470	.36	*R*	*R*	1.6	2.0	1.2
22	Memphis silt loam	.120	.205	.230	.239	.721	.28		*R*	5.6	3.2	2.9
23	Merced silt loam [e]	.945	.358	.260	.628	2.526	.22		6.7	3.6	2.1	4.0
24	Merrimac gravelly, sandy loam	[f].024	.012	.016	.004			*Z*	*Z*	*A*	*A*	*Z*
25	Miami clay loam	.034	.102	.097	.086				*Z*	0.9	*R*	*R*
26	Miami silt loam	.068	.074	.104	.076			*A*	*A*	1.0	0.6	0.8
27	Miller clay	.091	.148	.136	.083				*A*	1.2	1.0	.9

See footnotes at end of table.

TABLE 9.—*Corrosion of galvanized pipe and 16-gage steel sheet with nominal 2-ounce coatings*—Continued

Soil	Soil type	Rates of loss of weight (oz/ft²/yr)						Condition or rates of maximum penetration (mils/yr)				
		Pipe	Sheet			Bare [b]	Ratio [c]	Pipe B[d] (1.81)	Sheet			
		A (2.82) [a]	A3 (0.99)	B (0.01)	Y3 (1.07)				A	A3	B	Y3
28	Montezuma clay adobe	[f] 0.204	0.493	0.668	0.231	1.700	0.21		R	3.4	6.6	2.3
29	Muck	[f] .593	.515	.444	.421	1.467	.34	3.0	R	3.2	2.6	2.8
30	Muscatine silt loam	.045	.150	.135	.141			1.1	A	1.9	1.2	1.0
31	Norfolk sand	[f] .016	.005	.017	.005				Z	Z	A	Z
32	Ontario loam	[f] .056	.057	.058	.067	.284	.21	R	R	A	R	A
33	Peat	.172	.188	.401	.148	1.123	.20		R	1.6	2.7	1.3
35	Ramona loam	.030	.069	.105	.042			A	A	A	R	A
36	Ruston sandy loam	.023	.014	.043	.034				Z	A	0.4	A
37	St. Johns fine sand	.202	.314	.305	.301	.851	.35		R	2.0	1.7	1.4
38	Sassafras gravelly, sandy loam	[f] .020	.015	.021	.011				Z	A	A	A
40	Sharkey clay [e]	.092	.218	.220	.212	.742	.25	R	R	4.7	4.8	3.8
41	Summit silt loam	.051	.026	.036	.026			M	A	A	A	A
42	Susquehanna clay [e]	.071	.086		.074	1.059	.07		R	2.1		2.3
43	Tidal marsh	[f] .129	.102	.584	.064	1.185	.19	2.3	A	R	5.9	R
44	Wabash silt loam		.021	.071	.041					A	A	A
45	Unidentified alkali soil	[f] .174	.096	.160	.170	1.282	.12	3.6	R	1.8	0.5	1.5
46	Unidentified sandy loam	.016	.010	.016	.027	.416	.04	A	Z	Z	Z	Z
47	Unidentified silt loam	.100	.066	.078	.065			A	A	R	R	R

[a] The weight of coating given here is in ounces per square foot of exposed area. It is the average obtained from at least 10 measurements of thickness by the stripping method.

[b] In the column headed "Bare" are presented the average weight losses of rolled iron and steel specimens buried a similar length of time, i. e., approximately 10 years. These were not available for all soils.

[c] The column headed "Ratio" presents the ratio of the average of the first 4 columns of data to the bare-metal column, a low figure indicating that the galvanizing was effective in reducing weight loss.

[d] The B pipes were buried 12 years. They were not weighed before burial so weight losses are not known.

[e] In this soil there were 2 specimens. The condition or penetration is for the worst corroded specimen.

[f] There were 2 specimens of this material. The condition is for the worst of these specimens.

[g] No specimens 10 years old were removed from soil 35. The data given are for specimens exposed for 8 years.

In order to make the comparison of the materials simpler, data on the average rates of loss of weight for each material for three periods of exposure have been assembled in table 10. For the shortest period of exposure there seems to be no difference in the rates which can be attributed to differences in the weights of the coatings, probably because in most soils the losses were of zinc only. The open-hearth iron sheet showed the lowest average rate of loss. This is true also for the 8-year period of exposure, although the open-hearth iron pipe which carried a heavy coating showed the highest rate of corrosion. A possible explanation for this is that, in the case of the pipe, the zinc only was exposed, whereas the alloy layer was exposed on the sheets. The data for the 10-year period of exposure indicate that the rate of loss for galvanized materials decreases with increasing weight

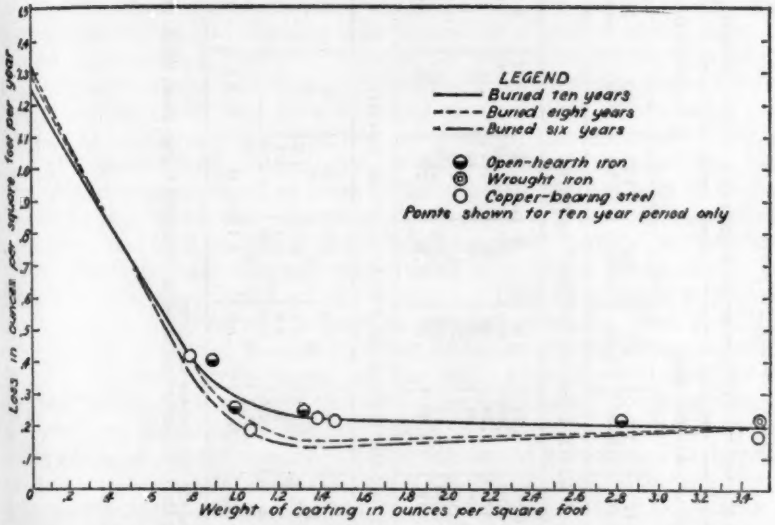

FIGURE 6.—*Correlation between rates of loss of weight and the weight of zinc on galvanized pipe and sheets exposed to six soils*

of coating within the range for which data are given. Beyond this range, the weight of coating has on the average no effect on the loss of weight, as shown in figure 6.

TABLE 10.—*Summary of data on specimens with nominal 2-ounce coatings*

Symbol	Material	Weight of coating [1]	Average rate of loss of weight (oz/ft²/yr)		
			6 years of exposure in 38 soils	8 years of exposure in 19 soils [2]	10 years of exposure in 39 soils
B	Bessemer steel sheet	0.81	0.091	0.145	0.169
A3	Open-hearth iron sheet	.99	.081	.128	.147
Y3	Copper-bearing steel sheet	1.07	.095	.133	.132
A	Open-hearth iron pipe	2.82	.091	.185	.113

[1] In ounces of coating per square foot of exposed area.
[2] The soils in this group are, on the average, more corrosive than those in the other groups.

TABLE 11.—*Effect of weight of zinc coating and character of base metal on rates of corrosion of galvanized pipe and sheet metal exposed for approximately 10 years*

[NOTE.—The numbers in parentheses are the weights (oz/ft²) of the coatings]

Soil	Galvanized pipe			Galvanized 16-gage sheet							Galvanized 18-gage sheet			Ungalvanized 18-gage sheet		
	A[1] (2.82)	*D* (3.48)	*Y* (3.47)	*A2* (0.90)	*A3* (0.99)	*A4* (1.33)	*Y2* (0.79)	*Y3* (1.08)	*Y4* (1.38)	*Y5* (1.46)	*CA* (0.94)	*CB* (0.83)	*CY* (1.06)	*CA-B* (0)	*CB-B* (0)	*CY-B* (0)
	RATES OF LOSS OF WEIGHT (oz/ft²/yr)															
13	0.086	0.10	0.12	0.34	0.22	0.18	0.27	0.14	0.10	0.17	0.076	0.057	0.075	0.57	0.53	*D*[2]
24	.024	.010	.004	.04	.012	.008	.004	.004	.004	.005	.021	.012	.009	.18	.17	0.17
28	.20	.28	.21	.20	.49	.52	.19	.23	.25	.34	.11	.10	*D*[2]	*D*	*D*	*D*
29	.59	.42	.30	.51	.51	.48	.44	.42	.37	.40	.47	.54	.35	*D*	.99	1.06
42	.071	.068	.054	.098	.086	.077	.12	.074	.10	.10						
43	.13	.17	.13	.44	.10	.086	.14	.064	.090	.077	.41	.57	.44	*D*	*D*	.88
45	.17	.20	.13	.81	.096	.12	1.29	.17	.40	.16	.38	.61	.31	*D*	*D*	*D*
	CONDITION OR RATES OF PENETRATION (mil/yr)															
13	*R*	*Z*	*A*	2.7	1.5	1.1	3.0	0.8	0.8	*R*	*R*	*R*	*R*	4.9+	4.9+	*H*
24	*Z*	*Z*	*Z*	*A*	*A*	*Z*	*R*	*Z*	*Z*	*Z*	*A*	*A*	*A*	2.3	2.7	2.7
28	*R*	*Z*	*A*	4.3	3.4	3.2	1.5	2.3	2.5	2.2	*R*	.4	*H*	*H*	*H*	*H*
29	*R*	*R*	*R*	4.1	3.2	2.5	3.9	2.8	2.5	2.4	1.7	5.0+	2.8	*H*	5.0+	5.0+
42	*R*	*A*	*R*	1.9	1.1	*A*	2.5	1.2	0.6	0.8						
43	*A*		*A*	5.5	*R*	*R*	1.5	*R*	*A*	.4	4.7+	4.7+	4.7+	*H*	*H*	4.7+
45	*R*	*Z*	*R*	6.0	1.8	2.0	*H*	1.5	2.1	*R*	2.8	4.7+	4.7+	*H*	*H*	*H*

[1] The meanings of the material designation symbols at the tops of the columns are as follows:
A=open-hearth iron; *D*=wrought iron; *Y*=copper-bearing steel; the *C* preceding another letter designates 18-gage sheet, the *B*, preceded by a dash, indicates that the specimen was not galvanized.

[2] The meanings of the condition symbols are as follows:
Z=Zinc still visible over entire surface of specimen.
A=Alloy layer exposed over at least a part of specimen but no rust.
R=Specimen rusty over at least a part of surface.
H=Hole entirely through specimen.
D=Specimen destroyed; impossible to determine weight loss.

Further light on the effects of the weight of the coating and of the base materials is afforded by table 11, which gives data on a variety of galvanized materials from seven soils. The data from this table are plotted in figure 6. The rates for the different base materials are differentiated by different symbols. Curves showing the trend of the data for other periods of exposure but without the points for the individual observations are shown by broken lines. The curves lie quite close together, and the differences between them probably lie within the standard errors of the tests. The point on the left end of the curve represents the average rate of loss for all ferrous pipe materials exposed to the same soils. This value was used because of the destruction of some of the thin sheet steel specimens. The figure indicates that the 10-year average rate of loss of weight of the galvanized specimens in the six corrosive soils was about one-fifth of that for ungalvanized specimens and that, during this period of exposure, the lightest weight of coating was almost as effective as the heaviest. It is to be expected, however, that as the period of exposure is lengthened the advantage of the heavier coating will become more evident. This is indicated by the data on rates of maximum penetration given in table 11. These show that the pipes which carried much more zinc than the sheets had no measurable pits, although most of the latter were pitted to a depth of at least 10 mils. The second part of table 11 also indicates that the heavy coating on the pipes afforded better protection to the base metal than did the lighter coating on the sheets.

The data for the 18-gage galvanized and black sheet show very definitely the superiority of the former. This illustrates a principle applicable to protective coatings in general, namely, that the life of unprotected material is short either because of the thinness of the material or the corrosiveness of the soil; a protective coating will probably increase the life of the structure sufficiently to justify its use. If, however, the life of the structure is long, the desirability of a coating is more questionable. Thus the use of galvanized rather than black corrugated iron culverts might be economical, although the use of large-diameter galvanized water pipes might not be advisable.

Galvanizing is extensively used on pipes up to about 4 inches in diameter. Many gas and water companies use galvanized pipe for house services. This coating is especially well adapted to this use because the pipe is installed by a few men in small and widely scattered jobs where the use of any coating equipment would be inconvenient and expensive. In a distribution system where all pipes are unprotected, most of the leaks will occur on services and small pipes because the pipe wall is relatively thin. The use of galvanizing on these pipes will tend to equalize the average life of large and small pipes. If electrolysis is the principal cause of leaks, galvanized coatings will be of little or no value. However, in small distribution systems where there are no street railways, and hence no electrolysis, and where the soils are moderately but not severely corrosive, galvanized coatings are perhaps the most economical means for reducing maintenance costs. Galvanized coatings for underground use should have a weight of at least 2 ounces of zinc per square foot of pipe surface.

The relative rates of corrosion of zinc, steel, and galvanized steel exposed to five soils for approximately 10 years are shown in table 12. These are the only soils in which zinc was placed. The table indicates

that for the period of exposure involved and for the soils for which comparisons can be made, zinc corroded less rapidly than iron or steel and that the galvanized steel corroded least of all.

TABLE 12.—*Rates of loss of weight and maximum pitting of miscellaneous metals and alloys buried for approximately 10 years*

Material	Soil									
	Hanford very fine sandy loam (*13*)		Muck (*29*)		Susquehanna clay (*42*)		Tidal marsh (*43*)		Alkali (*46*)	
	Loss[1]	Pits[2]	Loss	Pits	Loss	Pits	Loss	Pits	Loss	Pits
Zinc (thin)	0.35	4.0	0.46	3.9	0.085	1.7	0.23	3.3	*f*[3]	*f*
Do	.19	5.2	.38	*f*	.11	2.0	.45	3.7	*f*	*f*
Zinc (thick)	.34	7.0	.53	5.5	.078	1.8	.22	6.8	0.94	9.8
Open-hearth iron	.98	13.+	.58	6.2	.56	7.0	*f*	13.+	*f*	13.+
Copper-bearing steel	*f*	6.+	.69	6.+	.54	5.9	*f*	6.+	*f*	6.+
Galvanized steel sheet[4]	.14	.8	.42	2.8	.07	2.3	.06	*R*[6]	.17	1.5
Galvanized iron pipe[5]	.09	*R*	.59	*R*	.07	*R*	.13	*A*[7]	.17	*R*

[1] Loss is given in ounces per square foot per year.
[2] Rate of maximum penetration in mils per year.
[3] Failure, 1 or more holes (*f*). If this symbol appears in the loss column the specimens were corroded so badly it was not possible to weigh them.
[4] 16-gage copper-bearing steel sheet, 6 by 12 inches, coated with 2.15 oz of zinc per square foot of sheet.
[5] Open-hearth iron pipe, 2 by 17 in., coated with 2.82 oz of zinc per square foot of surface.
[6] Rusted, but no measurable pits; (*R*).
[7] Alloy layer exposed but not rusted: (*A*).

IV. MILL AND FOUNDRY SCALE AS PROTECTIVE COATINGS

Ferrous pipes as made at the foundry or mill are covered with an oxide coating commonly called foundry or mill scale. Various opinions have been expressed as to the effect of this scale on the corrosion of the pipe. Some believe that the scale acts as a protective coating, while others think that because the iron has been found to be anodic to mill-scale corrosion is accelerated at points where the scale is discontinuous. In 1926, specimens of several materials in their original condition and similar materials with the mill scale removed were buried in seven soils. Table 13 shows the rates of corrosion of these specimens after approximately 8 years of exposure. To facilitate the comparison of the materials with and without mill scale, the ratio of the number of cases in which the scale-free material was superior to the scale-coated specimens is given at the bottom of each part of the table. It is evident from the table that, on the whole, the specimens from which the scale had been removed corroded somewhat less than those having a coating of mill scale, i. e., that mill and foundry scale did not afford any protection to the specimens. In most instances there was so little difference between the rates of corrosion of the specimens with and without mill scale that the difference might be attributed to chance.

TABLE 13.—*Effect of mill and foundry scale on corrosion*

[Period of exposure was approximately 8 years]

Soil	Soil type	Pit cast iron		Delavaud cast iron		Steel		Wrought iron	
		A Normal	*MC* Machined	*C* Normal	*MD* Machined	*P* Normal	*M* Ground and polished	*K* Normal	*D* Rough ground
	RATE OF LOSS OF WEIGHT (oz/ft²/yr)								
9	Hanford very fine sandy loam	1.12	1.29	0.05	1.10	1.70	1.51	1.12	1.01
24	Merrimac gravelly sandy loam	.11	.13	.17	.16	-------	-------	.22	.18
28	Montezuma clay adobe	3.94	-------	1.14	-------	-------	-------	-------	-------
29	Muck	2.31	.99	5.28	1.27	1.21	1.06	1.18	1.22
42	Susquehanna clay	.70	.43	.59	.47	.89	.94	.88	.80
43	Tidal marsh	1.08	1.00	3.08	1.20	.86	1.14	.67	.67
45	Unidentified alkali	3.50	-------	3.55	2.59	2.64	2.26	2.51	2.17
	Ratio [1]	-------	3:5	-------	5:6	-------	3:5	-------	4:6
	RATE OF PENETRATION (mils/yr)								
13		17.8	12.8	7.8	9.1	19.3	15.3	11.9	11.1
24		3.6	3.2	3.8	2.4	-------	-------	4.7	3.8
28		20.4	-------	6.8	-------	-------	-------	-------	-------
29		11.4	5.0	10.7	8.9	10.5	9.8	6.3	7.3
42		17.9	15.9	7.0	8.9	8.8	10.0	10.3	9.4
43		14.1	5.2	27.5	11.5	10.8	8.1	15.3	9.7
45		22.3	-------	14.3	15.7	16.6	13.0	12.9	18.2
	Ratio [1]	-------	5:5	-------	3:6	-------	4:5	-------	4:6

[1] Ratio of cases of superiority to total number of cases of comparison.

V. PARKWAY CABLE

Specimens of parkway cable consisting of an insulated copper wire covered by a lead sheath followed by a wrapping of treated jute, two spiral wrappings of zinc-coated steel strip, and another covering of bitumen-impregnated jute, were buried in 47 test sites in 1922 and 1924.

This cable is usually laid in direct contact with the earth in rather shallow trenches. The coverings outside the lead sheath are largely for the purpose of protecting the cable against mechanical injury. The impregnation of the outer covering delays its decay but does not prevent the moisture reaching the metal beneath. The steel tapes are coated with zinc.

Table 14 indicates the conditions of the several components of the cable after approximately 12 years of exposure. It will be seen that although in many soils there was slight corrosion of the lead sheath no serious corrosion of the sheath occurred at any of the test sites.

TABLE 14.—*Condition of parkway cable buried from 10 to 12 years*

Ratings: *G*, good; *F*, fair; *B*, bad; *D*, destroyed; *P*, pitted; *R*, rusted; *SR*, slightly rusted; *BR*, badly rusted; *TW*, thin white corrosion product on lead sheath.

[All steel is zinc-coated]

Soil	Soil type	Outer fabric	Inner fabric	Outer steel[1] wrapper	Inner steel wrapper	Lead sheath
1	Allis silt loam	F	G	R	G	G
2	Bell clay	D	G	BR	R	TW
3	Cecil clay loam	D	F	P	R	G
5	Dublin clay adobe	B	G	SR	G	G
10	Gloucester sandy loam	D	G	P	R	TW
16	Kalmia fine sandy loam	D	G	P	SR	TW
17	Keyport loam	D	F	P	R	TW
18	Knox silt loam	B	G	R	SR	TW
19	Lindley silt loam	F	G	R	G	TW
24	Merrimac gravelly sandy loam	F	G	G	G	G
25	Miami clay loam	F	G	SR	G	TW
26	Miami silt loam	D	G	P	R	TW
28	Montezuma clay adobe	D	G	P	P	TW
29	Muck	B	F	P	G	TW
30	Muscatine silt loam	F	G	G	G	TW
31	Norfolk sand	D	G	BR	SR	TW
32	Ontario loam	D	G	R	G	TW
34	Penn silt loam	F	G	SR	SR	TW
35	Ramona loam	F	G	P	G	TW
36	Ruston sandy loam	B	G	P	R	TW
37	St. Johns fine sand	B	G	SR	SR	TW
38	Sassafras gravelly sandy loam	B	G	SR	G	TW
39	Sassafras silt loam	F	G	SR	G	TW
41	Summit silt loam	D	G	P	G	TW
43	Tidal marsh	B	G	R	SR	G
45	Unidentified alkali soil	B	F	R	R	G
46	Unidentified sandy loam	D	G	BR	R	TW
47	Unidentified silt loam	F	G	SR	SR	G

[1] All steel is zinc coated.

VI. MISCELLANEOUS NONMETALLIC COATINGS

Since the burial of specimens of protective coatings by the National Bureau of Standards in 1922, 1924, and 1926, and by the research associates of the American Gas Association and the American Petroleum Institute in 1929 and 1930, a number of quite different protective coatings have been developed. It was thought advisable, therefore, to give the manufacturers of these coatings an opportunity to have them tested under conditions which were severely corrosive with respect to steel pipe.

Ten kinds of nonmetallic coatings were submitted by manufacturers and buried in 15 corrosive soils, which differed greatly in their physical and chemical properties. Several of these coatings are experimental in nature and have not been offered to the public as protective coatings. The object of their manufacturers is to obtain data useful in the development of a satisfactory coating. The results of the tests are of interest to the public also because they show the ways in which soils affect protective coatings and indicate, therefore, some of the requirements for satisfactory coatings. A soil which rapidly corrodes steel is not necessarily destructive to protective coatings, and one that destroys certain kinds of coatings may not be corrosive. Since coatings are required only in corrosive soils, such soils should be used for testing coatings, and, to be helpful, reports on the performance of coatings should be accompanied by data on the corrosion of unprotected steel exposed to similar conditions.

The soil types in which the coatings were exposed and their locations are given in table 1. Some of the physical and chemical properties of these soils are given in table 2. Table 15 shows the identification letters for the coatings, together with a descriptive name for each. A more detailed description of the coatings follows. These descriptions were furnished by the manufacturers but in some cases are quite inadequate.

The following manufacturers furnished coatings for the tests:

American Machine and Foundry Co., Brooklyn, N. Y.
Ball Chemical Co., Pittsburgh, Pa.
Chadeloid Chemical Co., New York, N. Y.
Ferro Enamel Corp., Cleveland, Ohio.
P. D. George Co., St. Louis, Mo.
B. F. Goodrich Rubber Co., Akron, Ohio.
Goodyear Tire and Rubber Co., Akron, Ohio.
Harpoon Paint Products Inc., Long Island City, N. Y.
Irvington Varnish and Insulator Co., Irvington, N. J.
Thiokol Corp., Yardville, N. J.

TABLE 15.—*Nonmetallic coatings*

Identification letter	Descriptive name	Identification letter	Descriptive name
B	Synthetic rubber.	*G*	Hard rubber.
C	Vitreous enamel.	*H*	Loaded hard rubber.
D	Rubber paint.	*J*	Synthetic resin varnish.
E	Paint, unidentified.	*K*	Chlorinated rubber paint.
F	Cashew-nut oil-asbestos-fiber paint.	*W*	China wood oil-mica plastic.

The coatings listed in table 15 have been described by their makers as follows:

B.—A product described as an olefin-polysulfide reaction product. The specimens under observation were made by the addition to this product of small quantities of nine other materials to form a rubber-like substance. The dimensions of the specimens of this material are 10 by 5 by ¼ inch. They were placed on edge in the trench.

C.—A vitreous enamel coating described by the manufacturer as an acid-resisting enamel, free from pinholes. The thickness of the coating is approximately 14 mils.

D.—The manufacturer describes the coating as follows: first coat, 23-percent solution of rubber derivative in xylene; second and third coats, 30-percent solution of rubber derivative in xylene; fourth coat, 20-percent solution of rubber derivative in a mixture of turpentine and mineral spirits, plus 5 percent of carbon black as percentage of the total solids. The thickness of the coating was approximately 0.010 inch.

E.—Two applications of paint which differ in color. Neither the kind of pigment nor the kind of vehicle was specified. The thickness of the coating was approximately 0.005 inch.

F.—A semiplastic compound, which may be applied cold with a brush, consisting of 4½ parts of treated cashew-nutshell oil, 3 parts of fiber asbestos, and 3½ parts of mineral turpentine substitute. The thickness of the coating was approximately 0.006 inch.

Twelve of the specimens of coating *F* were placed in water for 1 week. Pattern tests [13] were then made. All tests indicated pinholes in the coating.

G.—A hard-rubber compound comprising rubber, sulfur, and an accelerator cured to a bone-hard condition. The thickness of the coating is about 0.09 inch. The bond between the pipe and the coating is not strong.

H.—Highly loaded hard-rubber stock containing 30 percent of magnesium carbonate and approximately 15 percent of "white substitute." The thickness of this coating is about 0.1 inch.

[13] S. P. Ewing and G. N. Scott, *An electrolytic method for determining the condition of nonmetallic pipe coatings.* Am. Gas Assn. Monthly **16**, 140 (1934).

J.—A modified synthetic resin applied to the pipe in the same manner as a paint or varnish. The pipe is then subjected to a baking operation at 425° F for 30 minutes. The thickness of this coating was about 0.002 inch.

K.—A paint coating containing imported highly chlorinated rubber which may be dissolved in solvents to which may be added drying oils, pigments, quartz meal, or carborundum. The exact ingredients of the coating, which was applied to the pipe 1 inch in outside diameter, were not stated. The coating was applied in Germany. Its thickness was approximately 0.006 inch.

W.—An experimental coating prepared as follows. The pipe was primed with a china wood oil varnish containing considerable lead and manganese drier as the vehicle. The pigment portion consisted of a mixture of equal parts zinc chromate, basic lead chromate, small proportion of oxide of zinc, and about 10 percent of inerts in the form of asbestine. This primer was baked at a temperature of about 200° F for ½ hour.

The coating consists of thoroughly dehydrated china wood oil to which was added powdered mica and a catalyst. This mixture was molded on the pipe and heated to 200° F for 3 hours. The thickness of this coating was about 0.17 inch.

Coatings G, H, J, and K were received after a part of the other specimens had been buried. The first two specimens were placed in eight soils and the last two, because of the limited number of specimens furnished, in only four soils. The results of all of the field tests on corrosion conducted by the National Bureau of Standards indicate that because of uncontrolled factors the data are likely to be erratic, and on this account a considerable number of observations are required, if reliable information is to be secured. Moreover, because of the wide differences in soils, a material suitable for one soil condition may be unsatisfactory in another. The results of observations on a few specimens in a few soils may, therefore, be misleading as to the general usefulness of the material tested.

The nonmetallic coatings differ so greatly in character that it is difficult to tabulate their conditions when removed from the test sites. The condition of the pipe to which the coating was applied is probably the best indication of the usefulness of the coating although the relative conditions of the specimens may differ for different periods of exposure.

Table 16 shows the conditions of the pipes after approximately 2 years of exposure. In most cases the conditions of two specimens of the same coating exposed to the same soil did not differ greatly. For this reason, and the fact that this report deals with a relatively short period of exposure of a small area, the condition of the worse of the two specimens is recorded in cases where differences occurred. It will be seen that, with two exceptions, the coated pipes were in better condition than the bare pipes in the same soil. On the other hand, no coating entirely prevented corrosion in all soils for 2 years, and on several specimens rather serious pits were found.

The last column of table 16 shows the condition of somewhat larger specimens of steel pipe protected for approximately 2½ years by an asbestos-fabric reinforced coal-tar enamel coating. This coating which is among the best of the bituminous coatings, can be obtained at reasonable cost and can be applied to any size pipe. The performance of better and worse bituminous coatings can be compared with the coatings in table 16 by reference to Technological Paper 368 and the reports of Scott [14] and Ewing.[15]

[14] G. N. Scott, *API coating tests—Progress report III.* Proc. Am. Petroleum Inst. 13, sec. 4, 114 (1932).
[15] S. Ewing, *AGA studies of coatings for pipe lines.* Proc. Am. Gas Assn. p. 741 (1933).

TABLE 16.—*Condition of pipe protected by nonmetallic coatings, after 2 years of exposure*

[The worse of the 2 specimens in each case is recorded]

The following symbols have been used to indicate the condition of the pipe. *U*=no corrosion; *R*=rusted; *M*=metal attack; pipe roughened by corrosion. The figures represent the depth of the deepest pit in mils (thousandths of an inch).

Soil	Soil type	Identification of coating										
		C Vitreous enamel	*D* Rubber paint	*E* Paint	*F* Cashew-nut oil-asbestos fiber	*G* Hard rubber	*H* Loaded hard rubber	*J* Synthetic resin	*K* Chlorinated rubber paint	*W* China-wood oil-mica compound	*N* Low-carbon steel tube	Asbestos felt and coal-tar enamel
61	Acadia clay	14	20	*M*	*R*	------	------	------	------	*R*	101	------
63	Cecil clay loam	*U*	*R*	*M*	*R*	------	------	*R*	16	*U*	37	*U*
65	Hagerstown loam	*U*	*R*	*M*	*R*	------	------	------	------	*R*	42	------
56	Lake Charles clay	*U*	40	------	*R*	------	------	------	------	*R*	26	------
57	Merced clay adobe	------	*M*	*M*	*R*	*U*	*U*	*M*	*M*	*U*	34	------
58	Muck	------	*M*	*M*	*R*	------	------	------	------	*R*	20	*U*
60	Peat	*U*	45	*M*	*R*	*U*	*U*	------	------	*U*	55	------
61	Sharkey clay	*U*	*U*	*R*	*R*	------	------	------	------	*U*	13	------
62	Susquehanna clay	*U*	*R*	*M*	*R*	------	------	------	------	*R*	68	*U*
63	Tidal marsh	*U*	*M*	------	*M*	------	------	------	------	*M*	21	*U*
64	Salinas clay	*U*	63	40	*R*	*R*	*U*	22	*M*	*U*	138	------
65	Alkali soil	*U*	*M*	45	*R*	*U*	*U*	------	------	*U*	43	*U*
66	Mohave sandy loam	*U*	*M*	28	*R*	*U*	*U*	------	------	*R*	71	------
67	Cinders	*U*	76	32	*R*	*U*	------	------	21	*U*	154+	*U*

In general, the thin coatings employing a volatile solvent were not as satisfactory as the thicker coatings. In the past, such coatings have been found to contain pinholes. It required four applications of the thin rubber solution to eliminate pinholes in coating *D*, and these applications proved ineffective in eliminating corrosion in more than one soil.

Since the strip *B* was not applied to a pipe its effectiveness as a coating can only be judged from the condition of the material. Seventeen specimens appeared to be unchanged by 2 years of exposure to soils. Eight specimens appeared to have become somewhat stiffer. In the tidal marsh, both specimens had hardened and showed minute surface cracks. Several specimens showed distortion resulting from unequal clod pressure on the two sides of the specimens.

Of the vitreous-enamel specimens, *C*, two pits were found on one specimen from Acadia clay, and one pit was observed on one specimen from muck. It is probable that these pits were the result of pinholes. All other specimens of enamel were unaffected.

Coating *D*, made from a solution of rubber, blistered badly in several soils, became quite brittle, and showed little adhesion to the pipe. Most of the specimens were rusted to some extent. Eight specimens showed pits 10 mils in depth or deeper. The coating material appeared to be in better condition than several others, which suggests the possibility that a satisfactory rubber-base coating could be developed.

Paint coating *E* gave results similar to paints that have been tested on other occasions. The color of many of the specimens changed.

A large percentage of the specimens developed a large number of small blisters beneath which rust was found.

Coating *F*, which is a cold application of cashew-nut shell oil and asbestos fiber, became brittle and rust formed beneath the coating. As a result the bond between the pipe and the coating was destroyed. Table 16 indicates that although the specimens rusted at all test sites no measurable pits developed within 2 years. Experience with other types of coatings indicates that thinly coated specimens which rust will develop pits on longer exposure.

Coatings *G* and *H*, which are hard-rubber compounds about 0.1 inch in thickness, behaved similarly. Several specimens showed rust near the ends of the specimens but no rust was observed elsewhere. The indications are that moisture entered at the ends of the specimens because of imperfect bond between the coating and the metal rather than through the coating. The continuity of the bond between the coating and the pipe is important. Experience has shown that it is very difficult to maintain a coating entirely free from voids and injuries until it has been placed underground. The adhesion of the coating to the pipe should, therefore, be such as to prevent moisture from spreading beneath the coating. Rusting which follows the entrance of moisture may crack the coating and allow more moisture to reach the pipe.

Coating *J*, a synthetic resin, was removed from only three soils. The coating exposed to Cecil clay loam (*53*) was only slightly affected. In the two alkali soils (*57* and *64*) to which the coating was exposed, it became brittle and rust formed on the pipe. In the Salinas clay (*64*) both pipes were pitted.

Specimens of the chlorinated rubber coating *K* were removed from four soils, but from two of the soils only one specimen was removed. The specimen removed from Cecil clay loam *53* was unaffected, except for two small pits about ½ inch apart, which may have been the result of imperfections or injury to the coating. The single specimen exposed to cinders (*67*) showed rust stains through the coating and rust in spots on the pipe. In the other soils, *57* and *64*, each of the specimens showed some small blisters.

Coating *W*, which is a compound of china wood oil and powdered mica, was the thickest coating tested. Seven of the coatings cracked longitudinally. As a few specimens were cracked when received it is possible that the cracking was the result of the aging of the material rather than an effect of the soil. The primer beneath the coating on most of the specimens was blistered. Since some of the blistered primers were covered by apparently perfect coatings, it is possible that the blistering of the primer was caused by the baking of the coating rather than by corrosion. Nine specimens showed rust spots but no measurable pits were found. The bond between the primer and the coating is poor. The rust inhibitor in the primer was not altogether effective.

In considering the significance of the data on nonmetallic coatings presented herewith, the reader should keep two facts in mind: (1) The data represent the condition of approximately ½ square foot of pipe surface, whereas the pipe-line operator is interested in the worst condition on thousands of square feet. As we are dealing with maxima, we should expect a section of pipe coated for test to show fewer rust spots and shallower maximum pits than would a whole pipe line to

which the same coating has been applied; (2) although protective coatings generally do not entirely prevent corrosion, they usually reduce the annual maintenance charges on the pipe line. It is possible that the use of an inexpensive coating may be more economical than the use of a more effective coating which costs more.

The final decision as to whether or not one or more of the coatings for which data have been presented can be used to advantage under a given soil condition depends not only upon the corrosiveness of the soil and the corrosion-inhibiting value of the coatings, but also upon the cost of the pipe, the cost of the coating and the cost of making repairs. It can be shown that in cases where the soil is very corrosive, almost any coating affords sufficient protection to pay for its cost. Between this condition and the one in which bare pipe will last indefinitely is a wide range of soil conditions for which corrosiveness, protective properties of coatings, and costs must be known before the engineer can determine whether or not any coating should be applied. For most of these cases sufficient data are not available.

VII. SUMMARY

1. With the exception of the lead-coated specimens, all of the coatings treated in this report appear to have reduced the rate of corrosion of steel during the period of the test.

2. None of the coatings have a perfect record for all specimens removed, although in some cases of short-time exposures the rusting of the protected pipe was probably caused by moisture entering through the ends of the specimens and not through the coating.

3. Specimens calorized by the powder process showed somewhat higher rates of loss of weight and somewhat lower rates of maximum penetration than those calorized by the dip process.

4. Lead is sufficiently corrodible in most soils to result in the perforation of lead coatings of the thickness used in these tests within 10 years. After the lead has been punctured, accelerated corrosion may occur because of differences of potential between lead and steel.

5. Over a 10-year period, the rates of loss of weight of galvanized steel were from one-half to one-fifth the rates for bare steel.

6. Galvanized steel corrodes most rapidly in poorly drained acid soils and in those high in salts.

7. For long periods of exposure, thick zinc coatings are superior to thin ones. A coating of 2.8 ounces per square foot of exposed surface prevented the formation of measurable pits in all but one soil for a period of 10 years.

8. The type of ferrous material to which the zinc is applied does not have an appreciable effect on the rate of corrosion of galvanized materials during the first 10 years of exposure.

9. The rate of corrosion of galvanized steel is lower than that of either zinc or steel alone.

10. Foundry and mill scale do not protect ferrous materials against underground corrosion.

11. The coverings over the lead sheath in parkway cable prevent serious corrosion of the sheath for a period of 12 years at least.

12. Of a group of nonmetallic and nonbituminous coatings, vitreous-enamel and hard-rubber coatings afforded the best protection over a 2-year period of exposure.

Thin coatings in this group permitted moisture to reach the pipe and rusting followed.

13. It is not possible to determine from the data presented whether or not any of the coatings would be advisable under any of the soil conditions studied because this is an economic problem depending largely on the cost of the coating and other factors.

The cleaning, weighing, and measuring of the specimens have been done mostly by A. L. Lewis and L. M. Martin. The inspection of the galvanized sheet and pipe was made by R. F. Passano of the American Rolling Mill Co., and C. P. Larrabee of the Carnegie-Illinois Steel Corporation. The inspection of the nonmetallic coatings was made by S. P. Ewing. Tables and drawings were prepared by L. M. Martin and R. W. Mattoon. From all of these men, and from I. A. Denison, many helpful suggestions as to the significance of the data have been received.

WASHINGTON, December 12, 1936.

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